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**THE QUANTUM
AND ITS INTERPRETATION**

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"By what way is the light parted?"

THE BOOK OF JOB

THE QUANTUM

AND ITS INTERPRETATION

BY

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WITH THIRTY DIAGRAMS



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PREFACE

MANY books have been written on the quantum theory and on its applications to special branches of physics, the work of Arnold Sommerfeld on *Atomic Structure and Spectral Lines*, in particular, being indispensable to all concerned with these subjects. The present volume is not a treatise on quantum theory, but an attempt to deal with the baffling problem of the nature of the quantum. Let it be said at once that no final solution of this problem has yet been reached; indeed some investigators would maintain that in the last analysis of all physical problems we must rest content merely with mathematical formulation. It is not at present possible to bridge the gap between the undulatory theory of light, which pictures the disturbance as a spreading wave, and the quantum theory of radiation which supposes the energy to be concentrated in bundles or "light units." It is still true, as Sir William Bragg said at the Robert Boyle lecture in 1921, that "we are obliged to use each theory as occasion demands." There seems hope, however, that some type of electromagnetic model, probably subject to suitable restrictions expressing quantum conditions, may serve to correlate the known facts of electricity, magnetism, and radiation. This anticipation receives support from the new undulatory or wave mechanics associated with the name of Schrödinger, of which an account is given in this volume.

It is becoming more and more evident that the electron must be regarded as the seat of a periodic process, and that particles of matter may themselves be spoken of as "waves." While this volume was passing through the press this view has been confirmed by the experiments of Davisson, who examined the reflection of electrons from a crystal, and of G. P. Thomson, who studied the scattering of a beam of electrons in passing through a thin crystalline plate. C. G. Darwin has discussed the theoretical aspects of the electron as a "vector wave."

The quantum theory has revealed an atomicity in nature of a kind previously unsuspected. This aspect of the theory, emphasized by Dr. J. H. Jeans in his first *Report on Radiation and the Quantum Theory* (1914), retains its mystery. But the

atomicity of electricity, in its dual aspect of positive and negative electrification, has also to be explained; and it may prove to be the case that these three types of atomicity represent only different aspects of some fundamental property of the electromagnetic field.

In this book emphasis has been laid on the magnetic aspect of the interpretation of the quantum. It is, of course, recognized that a complete theory must take into account both electric and magnetic forces; indeed, in the theory of relativity these become most closely linked together. The genius of Faraday led to the development of a mode of representing electric and magnetic fields by physical lines of force, and these may still serve a useful purpose in forming mental pictures of certain atomic phenomena, even though we may be driven eventually to employ the four-dimensional tubes of electro-magnetic force introduced by Prof. E. T. Whittaker. There is still much for the mathematician to accomplish in treating these "calamoids" as quanta.

The greater part of this work is based upon lectures delivered to advanced students in the University of St. Andrews. This accounts for the mode of presentation, for the somewhat detailed description of fundamental principles, and for occasional repetition. I have endeavoured to take a middle course between a mathematical and a purely descriptive treatment.

I wish to express my thanks to all those who have assisted me, and in particular to Mr. R. S. Maxwell, Mr. W. G. Robson and Dr. Ian Sandeman for help in the preparation of the manuscript or in reading the proofs. For permission to reproduce diagrams, or for the loan of blocks, my thanks are due to the Royal Society of Edinburgh, the Editor of *Nature*, the Editors of the *Philosophical Magazine*, Mr. C. H. Douglas Clark, Sir Alfred Ewing, Mr. H. Moore, Prof. Arnold Sommerfeld, and Drs. Goudsmit and Uhlenbeck. I am indebted to Prof. A. Fowler for tables showing the arrangement of electrons in atoms.

H. S. A.

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* Reproduced from "The Basis of Modern Atomic Theory" (Douglas Clark), Methuen & Co., Ltd.

† Reproduced from "Atomic Structure and Spectral Lines" (Sommerfeld), Methuen & Co., Ltd.

‡ Reproduced from "Proceedings of Royal Society of Edinburgh," by permission of the Secretary.

§ Reproduced from "Philosophical Magazine," by permission of the Editors.

PART I

FUNDAMENTAL FACTS AND PRINCIPLES

CHAPTER I

THE QUANTUM THEORY: PRELIMINARY SURVEY

The quantum theory . . . represents a complete departure from the old Newtonian system of mechanics.

We, as physical machines, are built on a scale which is large compared with the scale of light waves and electrons, from which it has resulted that our first physical experiments, as a race, have been concerned with matter also on a scale very large in comparison with its ultimate structure. The Newtonian laws have undoubtedly been found adequate to explain the whole series of what we may call large-scale phenomena, but no adequate reasons have, so far, been given for asserting that they must also be the laws which govern small-scale phenomena. The fact seems to be that the old laws are not, so to speak, fine-grained enough to supply the whole truth with regard to small-scale phenomena.

J. H. JEANS

To be living in a period which faces such a complete reconstruction of our notions as to the way in which aether waves are absorbed and emitted by matter is an inspiring prospect. The atomic and electronic worlds have revealed themselves with beautiful definiteness and wonderful consistency to the eye of the modern physicist, but their relation to the world of aether waves is still to him a profound mystery for which the coming generation has the incomparable opportunity of finding a solution.

R. A. MILLIKAN

1. Origin of the Quantum Theory

THE quantum theory, which has proved of such great importance in the study of Physics in the present century, originated in an attempt to account for the characteristic properties of the heat radiated from a hot body. We shall suppose that in the interior of such a body is a cavity, and that the body

is maintained throughout its substance and for an indefinite time at a constant temperature. Inside the cavity (Hohlraum) there will be a continuous stream of radiation in all directions. The problem of radiation is that of determining the way in

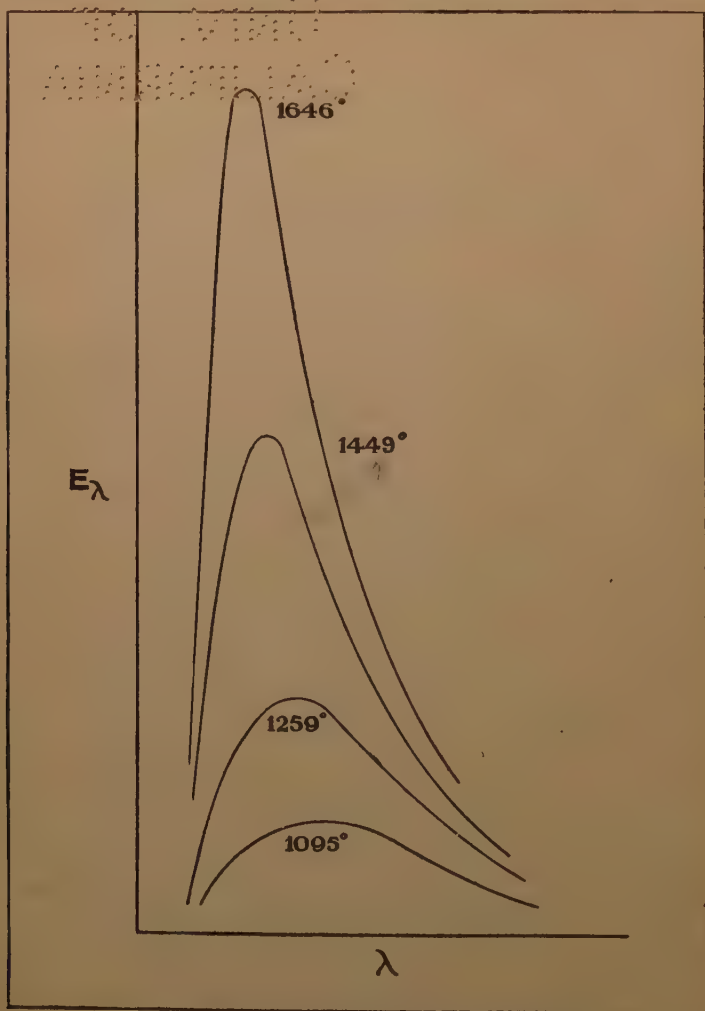


FIG. 1.—Energy and Wave-length of Radiation.
Temperatures are in degrees on the absolute scale.

which the energy is divided between the various wave-lengths or frequencies which go to make up the complete continuous spectrum of the full or "black body" radiation.

On the experimental side the problem has been solved with considerable accuracy by the concordant experiments of a

number of independent investigators. By heating the body to incandescence and allowing a beam of the radiation to issue through a *small* opening, the character of the radiation may be examined after it has been analysed in a spectroscope. It is found that there is a particular wave-length, λ , usually in or beyond the red part of the spectrum, corresponding to maximum energy of emission (Fig. 1).

On the theoretical side the problem presented great difficulties. If the laws of classical mechanics are true, there appears to be no escape from the conclusion that the whole of the energy ought to be found at the extreme ultra-violet end of the spectrum, no matter what may be the temperature of the enclosure. It was to meet this difficulty that Dr. Max Planck,* of Berlin, put forward his new theory in a communication to the German Physical Society on December 14, 1900. In this paper "On the distribution of energy in the normal spectrum," he described a new method of obtaining the formula, now known as Planck's formula,† which he had announced a few weeks earlier. In order to secure agreement with the experimental results he was compelled to introduce a new hypothesis which was quite inconsistent with the classical theory. It was not unreasonable to suppose that the hot body contained certain "vibrators" or "resonators" which could emit radiation, a simple harmonic oscillator of frequency ν being concerned in the emission of radiation of corresponding frequency. But the new and strange assumption was that such a vibrator could only possess energies $h\nu$, $2h\nu$, $3h\nu$. . . , where h is a constant, now known as Planck's constant.

This assumption is practically equivalent to saying that radiant energy E of any assigned frequency ν can be emitted and absorbed only as an integral multiple of an element of energy, that is

$$E = nh\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad 1 : 1\frac{1}{2}$$

where n is always a positive integer.

This may be called the hypothesis of "energy quanta," as it seems to imply the existence of a unit of energy $h\nu$; but it is hardly correct to say that the quantity $h\nu$ represents a universal "atom" of energy, since the amount depends on the frequency of the vibration considered. The numerical value of the quantum constant h deduced by Planck from his formula as applied to

* Max Planck, *Verh. d. deutsch. phys. Ges.*, vol. 2, p. 237, 1900; *Ann. d. Physik*, vol. 4, p. 553, 1901.

† Planck's radiation formula is given in Appendix III, p. 258.

‡ Mathematical equations are referred to by means of two numbers, of which the first is the number of the chapter, the second the number of the equation in the chapter.

the measurements of Kurlbaum and of Lummer and Pringsheim was

$$h = 6.55 \times 10^{-27} \text{ erg sec.},$$

a value which is in remarkably good agreement with later and more accurate determinations by various methods. The value adopted in this book is

$$h = 6.558 \times 10^{-27} \text{ erg sec.}$$

It will be noticed that h is a quantity of the dimensions of energy multiplied by time, i.e. of *action*, as the term is used in applied mathematics in connection with the Principle of Least Action.

The fundamental relation of Planck's theory may obviously be written in the form

$$\frac{E}{\nu} = nh \quad . \quad . \quad . \quad . \quad . \quad 1:2$$

ν being the frequency. The equation may also be written

$$E\tau = nh \quad . \quad . \quad . \quad . \quad . \quad 1:3$$

where τ is the period of the vibration. This may be interpreted by regarding E/ν or $E\tau$ as the action, and h as an element of action. From this point of view, which agrees closely with that adopted in the later developments of the subject, the quantum of action, h , is a universal constant, a true *atom* of action. We may gain some modicum of satisfaction from the idea that action is atomic, though as Jeans has remarked "an attempt to imagine a universe in which action is atomic leads the mind into a state of hopeless confusion!"

An alternative mode of regarding the quantum constant may be mentioned here. J. W. Nicholson,* in an investigation of the nebular and coronal spectrum, suggested that the angular momentum of an atomic system might be equated to $nh/2\pi$. Here $h/2\pi$ appears as a natural unit of angular momentum, the physical "dimensions" of this quantity being the same as those of action.

2. Photo-electricity

In 1905 Einstein† made a notable suggestion which has proved fruitful in predicting experimental results although it raises many grave difficulties. This was the hypothesis of the existence of "light quanta," an idea which has also been developed by J. J. Thomson in his unitary theory of light. According to

* J. W. Nicholson, *Monthly Notices, R.A.S.*, vol. 72, p. 677, 1912.

† A. Einstein, *Ann. d. Physik*, vol. 17, p. 132, 1905; vol. 20, p. 199, 1906.

this hypothesis, the energy of radiation is to be treated as though it were done up in bundles, the energy of the bundle or light quantum being given by Planck's expression $h\nu$. Further, only a single quantum is involved in any single physical change. This is sometimes known as Einstein's law, which may be stated as follows: "In every case where there is a mutual transformation between moving electrons and electromagnetic radiation, a single light quantum is utilized or is liberated."

One aspect of this reciprocal relation is seen in the photo-electric effect. When light of sufficiently short wave-length is allowed to fall upon a polished metal surface, negative electrons are set free with a velocity which depends upon the wave-length of the exciting light. The maximum kinetic energy of the electrons increases with frequency in accordance with a formula first suggested by Einstein in the paper referred to. Einstein's formula is:

$$\frac{1}{2} mv^2 = h\nu - P \quad . \quad . \quad . \quad . \quad . \quad 1:4$$

Here $\frac{1}{2}mv^2$ corresponds to the maximum kinetic energy of the emission; $h\nu$ corresponds to the energy of the light quantum, and P measures the work done when an electron escapes from the atom to which it is attached. It is found that this quantity P , which is called the "electron affinity," can be expressed as $h\nu_0$ where ν_0 is a definite frequency characteristic of the metal on which the radiation falls. The equation, which has been called "the fundamental law of photo-electric activity," now takes the form

$$\frac{1}{2} mv^2 = h(\nu - \nu_0) \quad . \quad . \quad . \quad . \quad . \quad 1:5$$

The kinetic energy of the electron is proportional to the difference between the frequency of light and the frequency characteristic of the particular metal.

The significance of the relation may best be appreciated by considering a particular case. For sodium the characteristic or "threshold" frequency is about 5.15×10^{14} vibrations per second, corresponding to green light. If the light is redder than this, it may fall on sodium for centuries without liberating any electrons, but if the light is bluer than the specified green light, it will at once bring about the separation of electrons and the maximum kinetic energy of emission will increase as the frequency increases. Einstein's equation has been verified by numerous experimenters—in the first instance by Hughes* and by Richardson and Compton,† then by Millikan‡ and his pupils—indeed Millikan's experiments based on this relation,

* A. L. Hughes, *Phil. Trans.*, vol. 212, p. 205, 1912.

† O. W. Richardson and K. T. Compton, *Phil. Mag.*, vol. 24, p. 575, 1912.

‡ R. A. Millikan, *Phys. Rev.*, vol. 7, p. 355, 1916.

furnish us with one of the most accurate methods of determining Planck's constant h . The equation possesses a very high degree of generality: it applies to ordinary light and to X-rays, and appears to be valid not only in the emission of electrons under the influence of light, but also when emission of radiation is brought about by the impact of electrons. Consider for example the production of X-rays in a Coolidge bulb. "A plentiful supply of electrons is provided at the cathode by heating a fine spiral of tungsten wire to a high temperature. A high potential difference between cathode and target is provided by some appropriate means, and the electrons are hurled at the target, each possessing an amount of energy equal to the product of the electron charge and the applied potential. Where the electrons strike, some of their energy is converted into electro-magnetic waves of very high frequency, the so-called X-rays. Suppose that we measure the energy supplied to each electron—not an easy matter with the usual arrangements, but very easily done if, as in certain experiments of Duane and Hunt at Harvard University, the potential is derived from a great storage battery of 40,000 volts. Suppose, further, that we analyse by the X-ray spectrometer the X-radiation that issues from the target. We find that the frequencies of the emitted rays may have a wide range of values, but that the upper limit of the frequencies is always proportional to the energy of the electron, and, therefore, to the potential imposed on the tube. This ratio remains the same no matter what the intensity of the electron discharge, and no matter what the nature of the target." The ratio is, in fact, Planck's constant h . Sir William Bragg, from whose Kelvin lecture * the quotation is taken, points out the reciprocal character of the relation in the case of X-rays, and emphasizes the extraordinary and, at present, insoluble problem involved. "It is not known how the energy of the electron in the X-ray bulb is transferred by a wave motion to an electron in the photographic plate or in any other substance on which the X-rays fall. It is as if one dropped a plank into the sea from a height of 100 feet, and found that the spreading ripple was able, after travelling 1,000 miles and becoming infinitesimal in comparison with the original amount, to act upon a wooden ship in such a way that a plank of that ship flew out of its place to a height of 100 feet. How does the energy get from one place to another?" "In many ways the transference of energy suggests the return to Newton's corpuscular theory. But the wave theory is too firmly established to be displaced from the ground that it occupies. We are obliged to use each theory as occasion demands and wait for

* *Nature*, vol. 107, p. 79, 1921.

further knowledge as to how it may be possible that both should be true at the same time."

3. The Photo-chemical Equivalent

Another illustration of Einstein's hypothesis is provided by his photo-chemical law: when light of given frequency is incident on a system sensitive to such light, for each single light quantum absorbed one molecule of the absorbing substance is decomposed. In other words, the number of molecules affected is equal to the number of light quanta absorbed. As Jeans points out: "The law not only prohibits the killing of two birds with one stone, but also the killing of one bird with two stones. Since the energy of a quantum $h\nu$ is proportional to its frequency ν we understand how a small amount of violet light can accomplish what no amount of red light would suffice to do, a fact familiar to every photographer—we can admit quite a lot of light if only it is red, but the smallest amount of violet light spoils our plates."

It must, however, be said that most photochemical processes are complicated by secondary reactions which make it extremely difficult to test the direct applicability of the law. It is now generally admitted that the absorbing molecule absorbs energy in quanta; but the number of molecules *decomposed* may differ considerably from the number of *absorbing* molecules. In a few reactions, and within certain narrow spectral limits, these numbers have been found the same. It is, then, extremely probable, if not certain, that the primary process consists in the absorption of an energy quantum; but the subsequent changes are frequently so complicated that it is not at present possible to express them in terms of the quantum theory.

Suggestions have been made by Trautz, Lewis, and Perrin that radiation is an important factor in all chemical action, Perrin in particular having developed the view that "ordinary" chemical reactions may be regarded as due to radiation, that is as photo-reactions. But the observed velocities of reaction are much in excess of those required (apparently) by this hypothesis. Although the radiation hypothesis is in some respects attractive, its supporters have not yet been able to present it in such a form as to make it rank as a theory capable of giving quantitative expression of the results of experiment. Indeed it would seem that far more attention than it has yet received should be paid to the effect of electron collisions in promoting chemical change.*

* "Photochemical Reaction in Liquids and Gases," Faraday Society Discussion, *Trans.*, vol. 21, p. 438, 1926.

4. The Quantum Theory of Spectral Series

The application of the quantum theory to the study of spectra continues to excite very great interest. This work, which will always be associated with the name of the Danish physicist Niels Bohr,* is based on two fundamental ideas. The first is a natural extension of the principle involved in the photo-electric effect. Bohr argued that when an atom emits monochromatic radiation of frequency ν , it must be because the atomic system has lost energy of amount $h\nu$. Thus

$$h\nu = H_a - H_e \quad . \quad . \quad . \quad . \quad . \quad 1:6$$

where H_a and H_e are the values of the energy in the two states † of the atomic system under consideration. This relation, generally known as Bohr's Frequency Condition, at once explains the Combination Law in connection with spectral series. This law states that the frequencies of the lines of a spectrum are given by the difference between pairs of terms of a sequence.

But a second application of the quantum principle is required to fix the "stationary states" of the atomic system, that is to determine the *permissible* orbits by "quantizing the orbits." In the earlier work this was effected by employing the suggestion of J. W. Nicholson that h may be regarded as a natural unit of angular momentum. The determination of the orbits is simple when a single electron is moving in the field of a positively charged nucleus.

By the application of these hypotheses Bohr was successful in deducing Balmer's and certain similar series emitted by hydrogen, and the enhanced spectrum of helium, i.e. the spectrum given by helium which has lost one electron so that there is a surplus positive charge. The same principles have also been employed in the explanation of the spectra of other elements.

In particular we must notice the remarkable agreement between the value of the fundamental Rydberg constant of spectroscopy deduced by Bohr and that found as the result of observation. Bohr's value for this fundamental frequency is

$$\nu_\infty = \frac{2\pi^2 me^4}{h^3} \quad . \quad . \quad . \quad . \quad . \quad 1:7$$

where e is the charge in ordinary electrostatic units, m is the

* Bohr, *Phil. Mag.*, vol. 26, pp. 1, 476, 857, 1913.

† It is convenient to use the subscript letters a and e to distinguish between the initial (antecedent) state and the final (end) state of the system.

mass of an electron, and h is Planck's constant. Taking the most recent determinations * of m , e and h , we find

$$\nu_{\infty} = 3.286 \times 10^{15} \text{ sec.}^{-1}.$$

Spectroscopic measurements of wave-lengths and a knowledge of the speed of light lead to the experimental value of Rydberg's constant, $\nu_{\infty} = 3.2906 \times 10^{15} \text{ sec.}^{-1}$.

But the matter does not end here. The results require slight modification in consequence of the fact that as the mass of the nucleus is not infinite, the nucleus itself must describe an orbit. When this is taken into account, it is possible to form an estimate of the ratio between the mass of the electron and the mass of the nucleus from spectroscopic observations of the lines of hydrogen and helium.

The discovery by C. G. Barkla of "fluorescent" X-radiation characteristic of a particular element and the distinction drawn by him between the harder "K" rays and the softer "L" rays prepared the way for a complete study of the spectrum of X-rays. Rapid progress in this branch of physics was made after the introduction of the X-ray spectrometer in which a crystal serves as a diffraction grating. In Bohr's theory the penetrating K radiation is attributed to the fall of an electron to the lowest atomic "level"—or the innermost "electron ring"—the "L" radiation being due to the fall of an electron to the "level" above this, corresponding to the next most stable position for an electron.

The application of the quantum theory to X-ray spectra has yielded results of great interest in connection with the structure of the atom, but the subject is too wide to enter upon here and the discussion of it may profitably be deferred.

5. The Generalized Quantum Theory

Further progress has been made possible by a later and more general formulation of the quantum theory put forward by W. Wilson, Sommerfeld, Ishiwara and several others, which has linked together the various interpretations given for the quantum constant. It is supposed that each physical system behaves normally in a conservative way, its motion being subject to Hamiltonian dynamics. It is then said to be in one of its stationary states. Interchanges of energy between physical systems are the result of catastrophes or revolutions in the atom. These interchanges are discontinuous in character and so involve the emission or absorption of an amount of energy depending on the initial and final state. The characteristic and funda-

* See Appendix II, p. 257.

mental hypothesis of the generalized form of the quantum theory is expressed in equations of this form :

$$\oint p dq = nh \quad . \quad . \quad . \quad . \quad . \quad 1 : 8$$

where q and p are Hamiltonian positional and impulse co-ordinates, and the symbol $\oint$ denotes that the integration is extended over a complete period corresponding to the co-ordinate q considered.

By employing these principles with relativistic extensions taking into account the dependence of the mass of the electron upon its velocity, Sommerfeld* has been able to explain and even to predict the fine structure of the lines in Balmer's series of hydrogen, and also in the enhanced helium spectrum.

On the basis of this theory an explanation has been given of the resolution of the hydrogen lines brought about under the influence of an electrostatic field. This was observed independently by Lo Surdo† and by Stark.‡

The corresponding case where the resolution is due to a magnetic field—the well-known Zeeman effect (Chapter XV)—has been discussed by Sommerfeld, Debye, Bohr, and others, and although a complete explanation of all the complexities observed has not yet been given, the cases normally occurring have been accounted for. "Here, the result of the quantum theory is identical with that from classical mechanics, and an inspection of the quantum equation shows that the quantum occurs on both sides and so divides out. This suggests that many phenomena which at present are thought to be satisfactorily explained by dynamics are really quantum phenomena, but that the quantum has divided out from the equations." §

6. Molecular Rotations

If the principles of the quantum theory be accepted, the important question arises as to how they are to be applied in connection with rotations, particularly rotations of molécules. The application of the theory to molecular rotations has been based, in some cases, on assumptions which render the results less secure than those derived in connection with other phenomena, but it seems certain that the clearer knowledge gained as to the generalized form of the theory will remove such ambiguities as still remain. In this connection the most important subjects are, first, the specific heats of gases having

* Sommerfeld, *Ann. d. Physik*, vol. 51, pp. 1, 125, 1916.

† Lo Surdo, *Accad. Lincei, Atti*, vol. 22, p. 664, 1913.

‡ Stark, *Preuss. Akad. Wiss. Berlin*, vol. 40, p. 932, 1913.

§ C. G. Darwin, *Brit. Assn. Report*, Section A, 1921.

molecules composed of two or more atoms, and second, the spectra of such gases, in particular the infra-red spectrum first investigated from this standpoint by Bjerrum.* The field of investigation offered by band spectra is a very wide one and within recent years results of great importance have been obtained.† Band spectra are the characteristic spectra of molecules containing more than one atom, but the quantum process is more complex than that in line spectra, since it involves changes in the state of rotation of the molecule and in the state of vibration of the atomic nuclei, as well as in the state of the excited valence electron. It is now recognized that between molecular and atomic electron transitions there is essential similarity. Further inquiry is sure to throw light on the difficult question of the structure of gaseous molecules, and already it is possible to calculate with precision the moments of inertia and vibrational frequencies of diatomic molecules from their spectra.

7. The Quantum Theory of the Solid State of Matter

It is not in connection with radiation only that the quantum theory has led to results of outstanding importance. The theory has been applied to the problem of the specific heat of matter in the solid state, and consequently new fields of investigation have been opened up in this department of Physics. The failure at low temperatures of the law of Dulong and Petit, which assigns a constant value to the product of atomic weight and specific heat, may be explained if we abandon here, as we have already done in dealing with radiation, the principle of the equipartition of energy and make use, in some form or other, of the idea of a quantum. Einstein ‡ in 1907 was the first to attempt to solve this problem by supposing that Planck's unitary theory of energy could be applied to the vibrational energy of the atoms of a solid. A more complete and satisfactory theory was put forward in 1912 by Debye,§ who, instead of assuming a definite frequency characteristic of a particular substance, imagined the solid capable of vibrating so as to yield a whole spectrum of frequencies from $\nu_0 = 0$ up to a maximum value ν_m , this maximum frequency being determined by the condition that the total number of degrees of freedom is equal to the known total number for the vibrating atoms. The vibrations

* Bjerrum, *Nernst Festschrift*, p. 90, 1912.

† See "Molecular Spectra in Gases," *Bulletin of the National Research Council*, December, 1926.

‡ Einstein, *Ann. d. Physik*, vol. 34, pp. 170, 590, 1911; vol. 35, p. 679, 1911.

§ Debye, *Ann. d. Physik*, vol. 39, p. 789, 1912.

he identified with the elastic solid vibrations of the body, and in this way was able to obtain remarkably good agreement between theory and experiment. Still better agreement was secured by a modification of Debye's theory proposed by Born and Kármán* who, instead of regarding the substance as a continuous elastic solid, considered it as an arrangement of atoms in a space-lattice.

8. Nernst's Heat Theorem

The Heat Theorem of Nernst,† first published in 1906 and now known as the third law of thermodynamics, stands in close relation to the quantum theory. According to the principle of the Conservation of Energy there is for any system a function U of the variables which characterize the system, chosen so that the negative value of U denotes the content of energy, the value of the function being constant during the transformation considered. The problem of finding the relation between U and the free energy, A , had long attracted attention. According to the theorem of Nernst, A and U must coincide at very low temperatures, and it follows that A is definitely fixed if U is known as a function of the temperature down to the absolute zero. In other words, the new theorem makes it possible to calculate the free energy from purely thermal quantities. Planck remarks that the theorem is equivalent to the statement that the entropy of a condensed phase (solid or liquid) vanishes at the absolute zero of temperature.

A large amount of experimental work has been carried out by Nernst and his fellow-workers with the object of testing and illustrating the new principle. The theorem has a wide field of application, especially in physical chemistry. It is of importance in connection with the law of specific heats at low temperatures, and has been employed in developing an equation of state for a pure solid. Nernst assumes that it is valid for gases of finite density and for solutions as well as for the condensed systems to which it was originally applied. It is used in the calculation of "chemical constants" and in dealing with the "degeneration" of ideal gases at very low temperatures.

9. Magnetism and the Quantum Theory

This review of the fields in which the quantum theory has been applied would be incomplete without some reference to the

* Born and Kármán, *Phys. Zeitschr.*, vol. 13, p. 297, 1912; vol. 14, pp. 15 and 65, 1913. Born, *Dynamik der Kristallgitter* (Teubner, 1915).

† Nernst, *The New Heat Theorem* (Methuen, 1926).

subject of magnetism (Chapter VII). Attempts have been made by several investigators to apply the theory to induced magnetism, and agreement of a qualitative character has been obtained but it cannot be said that either the theoretical or the experimental side of the subject is at present in a satisfactory condition. Theoretically there is something to be said for the introduction of the hypothesis of the magneton, as one of the ultimate constituents of atomic structure, but the direct experimental proof of the existence of such a constituent is, and is likely to remain, a matter of surpassing difficulty. When this hypothesis was first mooted, it met with considerable opposition, but recently the idea of a spinning electron has attracted marked attention, partly through the work of L. V. King,* based mainly on the classical electrodynamics, but even to a greater extent through the suggestions of two young Dutch physicists, Goudsmit and Uhlenbeck.† According to Bohr‡ the hypothesis of the spinning electron "promises to be a very welcome supplement to our ideas of atomic structure." Suggested by the analysis of the anomalous Zeeman effect, the electron with a quantized spin seems likely to explain many of the difficulties met with in the finer structure of spectra and the problems of atomic magnetism.

In his book on *Magnetism and Atomic Structure* (Methuen, 1926), E. C. Stoner has given a comprehensive account of magnetic phenomena, and of the attempts made to interpret them in terms of the quantum theory. But as his work was completed before the hypothesis of the spinning electron had been adequately discussed, he has only been able to refer to it in the briefest possible manner.

Of outstanding importance is the experimental verification by Gerlach and Stern of the theory of spatial quantization (Chapter VI) put forward independently by Sommerfeld and Debye. This theory leads to the surprising conclusion that an atom endowed with a magnetic moment can take up only certain definite orientations in a magnetic field. The experiments not only support the quantum, as opposed to the classical theory, but allow of an absolute determination of the value of the Bohr magneton.

10. Atomic Structure

Finally in our survey we come to the question of atomic structure, which is one of the outstanding problems of Physics

* L. V. King, *Gyromagnetic Electrons*, Carrier, Montreal, 1926.

† Goudsmit and Uhlenbeck, *Nature*, vol. 117, p. 264, 1926.

‡ Bohr, *Nature*, vol. 117, p. 265, 1926.

at the present time. As pictured by Bohr the atom is a solar system in miniature in which electrons are circling in rapid orbital motion about a massive nucleus. Does this picture represent the actual facts, or is it possible to substitute stationary electrons, or perhaps magnetons, so as to give an approximately statical model as imagined by A. L. Parson, or by Lewis, and subsequently by Langmuir? And supposing we have satisfactorily applied the quantum theory to the arrangement of the electrons in the atom, what are we to say as to its bearing upon the still more difficult question of the structure of the nucleus itself?

All these problems will have to be reviewed in the light of more recent work on the spinning electron and on the mathematical expression of the quantum theory by Heisenberg, Schrödinger and others. The new quantum mechanics is a severe mathematical discipline but it has already met with considerable success in explaining experimental facts, and it may be hoped that in course of time the mathematicians may be able to express the theory in a form more acceptable to the physicist.

According to Kramers:* "This work clearly demonstrates the limited applicability of a picture of atomic structure, in which the behaviour of the electrons inside the atom is visualized by orbits possessing definite kinematical properties." The atomic model of Bohr has, however, played such a prominent part in the development of the quantum theory, that it will be necessary to devote a large portion of our space to its consideration. For the guidance of the reader it may be said here that the present volume falls naturally into three divisions. Part I contains a general account of the physical phenomena with which we are mainly concerned, and shows how they are related to atomic theories in general, and to the quantum theory in particular. It is designed for the student who has little previous knowledge of the latter theory. Part II is of a more specialized character and deals with certain investigations and speculations of a less orthodox character. It may therefore be omitted by the reader who is interested only in following the well-trodden path of what may be termed the classical quantum theory. Part III is an attempt to show how the theory has developed in more recent times, and includes an account of the new quantum mechanics. The last chapter is a discussion of the views advanced as to the interpretation of the quantum, emphasis being laid on some of the philosophical aspects of the questions involved.

The reader of this volume will find in it much that is speculative, and probably much that will require revision as our knowledge increases, but it is the fascination of the unknown

* Kramers, *International Critical Tables*, vol. I, p. 47, 1926.

that has brought it into being: the unsolved problem may afford a greater interest than the most perfect theory.

REFERENCES

In Appendix I is given a list of books, for the most part in English, having reference to the quantum theory. The standard work on the subject is Sommerfeld's treatise on *Atomic Structure and Spectral Lines*. The beginner may prefer a more popular account such as that given in the books by Andrade, Clark, or Oliver Lodge. Reiche's *Quantum Theory* is a very useful book, and special mention must be made of the invaluable *Report* by Jeans.

MATHEMATICAL INTRODUCTION

The certainty of mathematics depends upon its complete abstract generality. But we can have no a priori certainty that we are right in believing that the observed entities in the concrete universe form a particular instance of what falls under general reasoning.

Mathematics is a system of symbolic logic constituting a machinery for the evolution of results to which the finite unaided human intellect could not otherwise attain.

1. The Linear Harmonic Oscillator

[illegible]

16

represent the state of the system at any particular instant of time.

The equation of motion may be written

$$\frac{d^2 q}{dt^2} + \frac{\mu}{m} q = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad 2:2$$

or $\frac{d^2q}{dt^2} + \omega^2 q = 0$ 2:3

where $\omega^2 = \frac{\mu}{m}$. For our present purpose the solution of the equation may be written in the form

$$q = a \cos (\omega t - \varepsilon) \quad . \quad . \quad . \quad . \quad . \quad 2:4$$

where the constants of integration a and ϵ determine the *amplitude* and the *phase* of the vibration, respectively. The quantity $\omega = 2\pi\nu$, and is the number of complete vibrations in 2π seconds. It is often convenient to have a special name for this quantity, and following Albert Campbell, it may be called the *pulsatance* of the motion. The French call it "pulsation." The momentum p , may be written

$$p = m \frac{dq}{dt} = -m a \omega \sin(\omega t - \epsilon) \quad . \quad . \quad 2:5$$

We may easily deduce the relation between p and q from the two equations 2:4 and 2:5 in the form

$$\frac{p^2}{(ma\omega)^2} + \frac{q^2}{a^2} = 1 \quad . \quad . \quad . \quad 2:6$$

This result gives us a very convenient geometrical representation of the state of the resonator. We take q and p to represent rectangular Cartesian co-ordinates in a q - p plane (the so-called "state"-plane or "phase"-plane). Each point of this plane may be regarded as corresponding to some assigned momentary condition of the resonator.

The equation between p and q may be written in the form

$$\frac{q^2}{a^2} + \frac{p^2}{b^2} = 1 \quad \dots \dots \dots 2:7$$

(where $b = ma\omega$) and represents an ellipse. For different amplitudes we have a number of similar and similarly situated ellipses.

Consider next the energy of the system. It will be partly kinetic energy, $T = \frac{1}{2}m\left(\frac{dq}{dt}\right)^2$, and partly potential energy, V . The latter is equal to the work done against the restoring force

μq in a displacement q , so that $V = \int_0^q \mu q dq = \frac{1}{2} \mu q^2$. The total energy is given by

$$T + V = \frac{1}{2} m \left(\frac{dq}{dt} \right)^2 + \frac{1}{2} \mu q^2 \quad . \quad . \quad . \quad 2:8$$

The sum of the two terms on the right is $\frac{1}{2} \mu a^2$, or $\frac{1}{2} m a^2 \omega^2$, the total energy $T + V$ being therefore constant. Since the area A of the corresponding ellipse is πab , we find $\pi m a^2 \omega = A$ so that the energy can be written in the form $\frac{A \times \omega}{2\pi}$ or $A\nu$ where ν is the frequency.

In Planck's first theory the only possible stable condition of a resonator is one in which its energy is an integral multiple

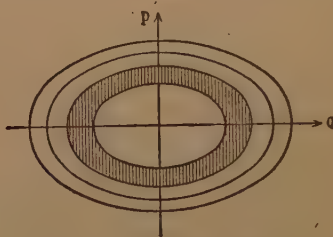


FIG. 2.—The Phase Plane.

of $h\nu$. Hence, A the area of the ellipse must be an integral multiple of h , so we may write

$$A = nh,$$

where n is a whole number. Thus according to the present theory the phase-plane may be divided up by a series of concentric ellipses such that the area between any pair of consecutive curves is equal to h , Planck's constant. The representative point of a resonator must always lie on one of the elliptic curves which form the boundaries between the regions of equal area (Fig. 2). When a resonator either emits or absorbs energy, the representative point jumps from one ellipse to another.

In the case of emission, the point leaps from the ellipse corresponding to its stationary state to a smaller ellipse; in the case of absorption the point jumps to a larger ellipse. Consequently both emission and absorption take place in multiples of the quantum $h\nu$.

The geometrical mode of representation here employed may be compared with the method in statistical dynamics in which the co-ordinates determining the position and velocity of a molecule are considered as determining the position of a point in an imaginary space of the appropriate dimensions. The

present case is the simplest of all because it is assumed that the directions of vibration of the resonators are perpendicular to a fixed plane, and that the resonators themselves are fixed ; thus two co-ordinates are sufficient to determine the condition of a resonator and the phase-space is of two dimensions only.

2. The Fundamental Equations of Classical Dynamics

The case of the simple resonator just considered may be used to illustrate certain dynamical principles of fundamental importance. The kinetic energy is, as we have seen,

$$T = \frac{1}{2}m\left(\frac{dq}{dt}\right)^2$$

It may also be written $T = \frac{1}{2}p\frac{dq}{dt}$, because $p = m\frac{dq}{dt}$; or it may

be written $T = \frac{p^2}{2m}$.

We notice that

$$2 \int T dt = \int p dq \quad . \quad . \quad . \quad . \quad 2:9$$

The latter integral is to be taken along the boundary curve. The expression on the left is an important quantity called the *characteristic function*, or the *action* of the system in passing from its position at a given instant to its position at a subsequent instant. That is, to find the action we integrate the kinetic energy with regard to the time between two assigned instants, or if we prefer it, we integrate $p dq$ between the two conditions corresponding to those instants.

The equations of classical dynamics may be summarized in the Principle of Least Action, according to which the actual motion of a dynamical system is such that the action is a minimum. Here it is assumed that the action is capable of continuous variation.

A *Conservative System* is such that if, after the system has undergone any series of changes it is brought back in any manner to its original state, the whole work done by external agents on the system is equal to the whole work done by the system in overcoming external forces. Such a system is distinguished from a *Dissipative System* in which the energy available for work becomes gradually degraded to less available forms by frictional agencies. (Clerk Maxwell, *Matter and Motion*, Chapter V.)

In a conservative system the potential energy, V , is the work done by the external forces in a displacement of the system from any assigned configuration to the standard configuration.

not explained. For this reason Planck modified the exposition of his theory, and introduced the conception of a *quantum of action*. His statement of this new point of view, derived from a study of statistical mechanics and probability may be paraphrased as follows :

"The probability of a continuous variable may be obtained by considering independent elementary regions, of equal probability. . . . In finding these elementary regions in classical dynamics, use is made of the theorem that two physical states, of which one is the necessary effect of the other, are equally probable. In a physical system, where q represents one of the generalized co-ordinates, p the corresponding 'moment' or 'impulse,' according to the theorem of Liouville the region

$\iint dp dq$ considered at any instant, is an invariant with respect to the time, if q and p vary according to Hamilton's equations. On the other hand, p and q can, at a given instant, take all possible values, independently of one another. Hence it follows that the elementary region of probability is the infinitely small element of the phase space $dp dq$. The new hypothesis has the effect of limiting the variability of p and q in such a way that these variables change only by jumps. . . . In this way the number of elementary regions of probability is reduced, whilst the extent of each is increased. The hypothesis of quanta consists of supposing that these regions, which are all equal, are no longer infinitely small but finite, and that for each

$$\iint dp dq = h \quad . \quad . \quad . \quad . \quad 2:14$$

where h is constant."

4. The Generalized Form of the Quantum Theory

Recent progress in the development of the quantum theory has been based on the generalized form of the theory put forward independently in 1915 by W. Wilson,* and by Sommerfeld.† A generalization of a somewhat similar character was proposed about the same time by Ishiwara,‡ but this contained certain features which are not altogether acceptable. The aim in all these methods is to furnish a common basis on which the theories of full (black body) radiation, spectral series and other pheno-

* W. Wilson, *Phil. Mag.*, vol. 29, p. 795, June, 1915.

† Sommerfeld, *Sitz. Ber. der Münchener Akad.*, Dec. 1915; *Ann. d. Physik*, vol. 51, p. 1, 1916.

‡ Ishiwara, *Tokyo Sugaki-Buturigakkwai Kizi*, 2nd ser., vol. 8, No. 4, p. 106.

mena may be established. The first two hypotheses of the Wilson-Sommerfeld theory may be stated shortly as follows:

(1) During certain intervals each dynamical system behaves as a *conservative* one. Between these intervals are relatively very short periods, during which definite amounts of energy may be emitted or absorbed. The interchanges of energy are "catastrophic" or discontinuous in character.

(2) The motion of a system in the intervals between such discontinuous energy exchanges is determined by Hamiltonian dynamics as applied to conservative systems.

The final and characteristic hypothesis of the theory cannot be stated briefly without some preliminary explanation. We have seen earlier that the condition of a dynamical system can be described by means of the Hamiltonian variables, $q_1, q_2 \dots, p_1, p_2 \dots$, where a variable such as q_k is known as a positional co-ordinate, and a variable such as p_k as an impulse co-ordinate (momentum). The kinetic energy, T , expressed as a function of $\dot{q}_1, \dot{q}_2 \dots$, and $q_1, q_2 \dots$, is homogeneous and of the second degree in $\dot{q}_1, \dot{q}_2 \dots$. If T contains products $\dot{q}_r \dot{q}_s (r \neq s)$, Wilson supposes such terms to have been removed by a suitable substitution, so that the kinetic energy may be assumed to have the form

$$T = \frac{1}{2}A_1\dot{q}_1^2 + \frac{1}{2}A_2\dot{q}_2^2 + \dots + \frac{1}{2}A_k\dot{q}_k^2 + \dots \\ \equiv T_1 + T_2 + \dots + T_k + \dots \quad \dots \quad 2:15$$

Further

$$2T = \dot{q}_1 \frac{\delta T}{\delta \dot{q}_1} + \dot{q}_2 \frac{\delta T}{\delta \dot{q}_2} + \dots + \dot{q}_k \frac{\delta T}{\delta \dot{q}_k} + \dots \quad \dots \quad 2:16$$

and consequently, since $p_k = \frac{\delta T}{\delta \dot{q}_k}$,

$$2T_1 = \dot{q}_1 p_1, \quad 2T_2 = \dot{q}_2 p_2 \dots \quad 2T_k = \dot{q}_k p_k \dots \quad \dots \quad 2:17$$

so that $2 \int T_1 dt = \int p_1 dq_1$ and so on.

It is assumed that the system in one of its steady states has a period, $1/\nu_1$, corresponding to $\dot{q}_1$, a period, $1/\nu_2$, corresponding to $\dot{q}_2$, etc.

Wilson's third hypothesis is that the discontinuous energy exchanges always occur in such a way that the steady motions satisfy the equations

$$\left. \begin{aligned} I_1 &\equiv 2 \oint T_1 dt = \oint p_1 dq_1 = n_1 h \\ I_k &\equiv 2 \oint T_k dt = \oint p_k dq_k = n_k h \end{aligned} \right\} \quad \dots \quad 2:18$$

where $n_1, n_2 \dots, n_k \dots$ are positive integers (including zero)

and the integration is extended over the values p_k and q_k corresponding to the period $1/\nu_k$. The factor h is Planck's universal constant.

Now T_k represents the instantaneous value of the part of the kinetic energy associated with the co-ordinate q_k . The integral $I_k \equiv 2 \oint T_k dt$ represents the corresponding amount of action. Thus the equations represent the fact that the action for each co-ordinate of the kind considered, when reckoned for the period appropriate to that co-ordinate, is an exact multiple of Planck's constant of action. Or the result may be expressed by saying that the *time average* of the part of the kinetic energy corresponding to q_k , estimated over a period $1/\nu_k$ is

$$\nu_k \oint T_k dt = \frac{1}{2} n_k h \nu_k.$$

Denoting this time average by $\bar{T}_k$, we have

$$2\bar{T}_k = n_k h \nu_k,$$

or

$$\frac{2\bar{T}_k}{\nu_k} = n_k h,$$

Simple illustrations of the general principles are afforded by systems possessing only one degree of freedom. In these cases the quantum condition may be written

$$I = 2 \oint T dt = \oint p dq = nh,$$

and the mean value of the kinetic energy taken over a period is $\frac{1}{2}nh\nu$, where ν is the frequency of the system.

(1) *Planck's Linear Oscillator.* We have already considered this particular system and we have seen that the mean value of the kinetic energy in one complete vibration is equal to the mean value of the potential energy, and it follows that as the mean value for the kinetic energy is $\frac{1}{2}nh\nu$ that must also be the value for the potential energy. Therefore the total energy of the resonator is $nh\nu$ in accordance with Planck's original statement of his theory (equation 1 : 1).

(2) *The Rotator.* This name has been suggested by Sommerfeld to describe a simple system in which a particle of mass m , charge e , is describing a circle about a fixed centre where there is a charge of opposite sign E (Fig. 3, p. 24).

This is the dynamical model used by Bohr in connection with the hydrogen atom. In this case the position of the moving particle may be determined by a single co-ordinate, which we may take conveniently as the angle AOP, or ϕ . This angle corresponds to the positional co-ordinate q . The velocity of the moving point is $v = a\dot{\phi}$ and the kinetic energy is

$$T = \frac{1}{2}mv^2 = \frac{1}{2}ma^2\dot{\phi}^2.$$

The linear momentum is $ma\dot{\phi}$, and the angular momentum is

$ma^2\ddot{\phi}$. This angular momentum is taken as the impulse co-ordinate p , so that $p = ma^2\dot{\phi}$ and is constant, for we are assuming a constant speed throughout the motion. Also $p = \frac{\delta T}{\delta \dot{\phi}}$, in accordance with equation 2:13.

The action may be written in the equivalent forms

$$I = 2 \oint T dt = \oint p dq$$

$$\text{or } I = \int_0^{2\pi} ma^2 \dot{\phi} d\phi = \int_0^{2\pi} ma^2 \dot{\phi} d\phi \quad . \quad . \quad . \quad 2:19$$

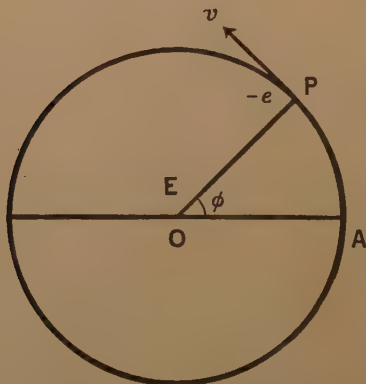


FIG. 3.—The Simple Rotator.

the integration extending over one complete period. Now $ma^2\dot{\phi}$ is constant and equal to p , therefore

$$I = \int_0^{2\pi} ma^2 \dot{\phi} d\phi = p \int_0^{2\pi} d\phi = 2\pi p \quad . \quad . \quad 2:20$$

The quantum condition is $I = nh$, so we get

$$2\pi p = nh$$

or

$$p = \frac{nh}{2\pi} \quad . \quad . \quad . \quad 2:21$$

as given by Nicholson and assumed by Bohr. Further, the kinetic energy of the system (which is numerically equal to the quantity called W by Bohr) is $\frac{1}{2}nh\nu$.

Returning to the general case, each pair of variables q_k, p_k , may be represented by rectangular co-ordinates in a plane, and it is a direct consequence of our third hypothesis (p. 22) that the condition of the system at any given instant during its steady state will be represented by a point on a certain locus

in each (q, p) plane. These loci divide all the planes into *equal* areas

$$\iint dp dq = h.$$

The representative points of a system *in its steady state* are always on the boundaries between these regions of equal area. When a *discontinuous* energy exchange takes place, the representative point jumps abruptly from one boundary to another.

We see that, as Sommerfeld graphically puts it, the "phase-space" is interwoven by the curves of the stationary states as by the meshes of a net. The size of the mesh is determined by Planck's constant, h .

It must be noted that it is only in special cases that the energy of the general dynamical system can be expressed as the sum of a series of terms such that each term contains only a single positional and impulse co-ordinate (q_k, p_k) . In such a case p_k can be expressed in terms of the corresponding q_k , and what is known as "separation of the variables" can be effected.

We have seen that Wilson, Sommerfeld and later Epstein and Debye laid down the condition that the integrals of the type $I_k = \oint p_k dq_k$ must be equal to exact multiples of Planck's constant. Schwarzschild* has put the quantum formulae into another form which is far more general. He supposes that by means of certain transformations the original co-ordinates and momenta (q, p) may be expressed as functions of a new system (Q, P) , possessing the following properties:

1. The quantities Q are *linear* functions of the time;
2. The quantities P are constants;
3. The quantities q and p are periodic functions of the quantities Q with a period 2π .

The variables Q are called "angular variables" ("Winkelkoordinaten"). The quantum formulae are

$$\int_{\square}^{2\pi} P_k dQ_k = 2\pi P_k = n_k h + \text{constant}.$$

If the character of the system is such that the variables can be separated, it is always possible to introduce angular variables. Burgers† has shown that the possibility of introducing angular variables is not so limited as had at first been supposed.

5. Adiabatic Invariance

The quantum conditions impose restrictions on the motion of a system so that only certain motions are "allowed." These

* Schwarzschild, *Sitz. Ber. Berl. Akad.*, p. 548, 1916.

† Burgers, *Proc. K. Akad. Amsterdam*, vol. 20, p. 163, 1918.

motions represent the "stationary states" of the system. Instead of stating the quantum conditions in mathematical form,* there is considerable advantage in presenting them in such a way as to lay the emphasis on their physical foundations. There are two fundamental physical principles underlying the standard quantum conditions, and these have proved of the greatest importance in the development of the quantum theory. They are the correspondence principle of Bohr, to be discussed in a later chapter, and the principle of slow mechanical transformability, developed by the work of Einstein, Ehrenfest, and Burgers. From an analogy with the adiabatic transformation of radiation the latter principle is often called the "adiabatic principle" of Ehrenfest.

Consider a dynamical system in one of its stationary states and suppose that an external field of force is applied to the system. When the field of force has reached its final value, the character of the motion will be altered and the final "allowed" state of the system must be such as is permitted by the quantum conditions for that final value.

As an illustration we may think of a hydrogen atom for which the quantized orbit will be altered in shape by the application of an electric field.

Instead of supposing that the field of force is applied suddenly, we may imagine that it is altered uniformly and very slowly until it assumes the final value. The system is then said to be "adiabatically affected." "The principle of mechanical transformability states that the standard quantum conditions are of such a nature that the process of adjustment then takes place in accordance with the equations of conventional mechanics, provided the number of intrinsic frequencies does not change." This means that *quantized orbits react classically to slowly changing conditions*. Any quantity depending on the motion which does not change its value when the motion is "adiabatically affected," is called an "adiabatic invariant."

For example, the quantity $2\bar{T}/\nu$, considered on page 23, is an adiabatic invariant. Again, for the hydrogen atom affected by a changing electric field, the moment of momentum about a line parallel to the lines of force is an adiabatic invariant.

Several interesting applications of the adiabatic hypothesis are given in Sommerfeld's *Atomic Structure and Spectral Lines*, page 304, where it is shown how problems in connection with the

* In addition to the Wilson-Sommerfeld method of stating these conditions, other modes of formulation have been employed, such as those of Schwarzschild (amplified by Bohr) and Trkal. See J. H. Van Vleck, *Quantum Principles and Line Spectra* (1926).

Stark effect and the Zeeman effect can be solved by its aid in a comparatively simple fashion.

REFERENCES

A good elementary account of the Principle of Least Action is given by Jeans in *Theoretical Mechanics* (Ginn and Company, 1907); a more detailed description of Hamiltonian dynamics is to be found in Routh's *Advanced Rigid Dynamics* or in Whittaker's *Analytical Dynamics*. Applications to the quantum theory are discussed in Max Born's *Mechanics of the Atom* and in Van Vleck's *Quantum Principles and Line Spectra*.

CHAPTER III

ATOMICITY IN ELECTRICITY AND MAGNETISM

If we accept the hypothesis that elementary substances are composed of atoms, we cannot avoid the conclusion that electricity, positive as well as negative, is divided into definite elementary proportions which behave like atoms of electricity.

HELMHOLTZ ON FARADAY'S LAWS OF ELECTROLYSIS

According to Ampère's theory, therefore, all the phenomena of magnetism are due to electric currents, and if we could make observations of the magnetic force in the interior of a magnetic molecule, we should find that it obeyed exactly the same laws as the force in a region surrounded by any other electric circuit.

CLERK MAXWELL, *Electricity and Magnetism*,
vol. ii, p. 419, 1873

It is, perhaps, possible to explain the cause of the most irregular magnet by theoretically bending such small currents in the direction required.

FARADAY, *Experimental Researches*, vol. ii, p. 145, 1844

1. The Electron Theory

IN Michael Faraday's *Experimental Researches in Electricity*,* the laws of electrolysis are clearly stated. These point to an atomic theory of electricity. Section 13 bears the suggestive title, "On the Absolute quantity of Electricity associated with the particles or atoms of Matter." The whole Section is extremely interesting, but special attention may be directed to paragraphs 852 and 869.

852. Although we know nothing of what an atom is, yet we cannot resist forming some idea of a small particle, which represents it to the mind; and though we are in equal, if not greater, ignorance of electricity, so as to be unable to say whether it is a particular matter or matters, or mere motion of ordinary matter, or some third kind of power or agent, yet there is an immensity of facts which justify us in believing that the atoms of matter are in some way endowed or associated with electrical powers, to which they owe their most striking qualities, and amongst them their mutual chemical affinity. As soon as we perceive, through the teaching of Dalton, that chemical powers are, however varied the cir-

* Vol. I, p. 195, seventh series, 1834.

cumstances in which they are exerted, definite for each body, we learn to estimate the relative degree of force which resides in such bodies : and when upon that knowledge comes the fact, that the electricity, which we appear to be capable of loosening from its habitation for a while, and conveying from place to place, *whilst it retains its chemical force*, can be measured out, and being so measured is found to be as *definite in its action* as any of *those portions* which, remaining associated with the particles of matter, give them their *chemical relation* ; we seem to have found the link which connects the proportion of that we have evolved to the proportion of that belonging to the particles in their natural state.

869. The harmony which this theory of the definite evolution and the equivalent definite action of electricity introduces into the associated theories of definite proportions and electro-chemical affinity, is very great. According to it, the equivalent weights of bodies are simply those quantities of them which contain equal quantities of electricity or have naturally equal electric powers ; it being the ELECTRICITY which *determines* the equivalent number, *because* it determines the combining force. Or, if we adopt the atomic theory or phraseology, then the atoms of bodies which are equivalents to each other in their ordinary chemical action, have equal quantities of electricity naturally associated with them. But I must confess I am jealous of the term *atom* ; for although it is very easy to talk of atoms, it is very difficult to form a clear idea of their nature, especially when compound bodies are under consideration.

Thus Faraday's laws of electrolysis point clearly to an atomic view of the constitution of electricity. This fact was emphasized by Helmholtz in a celebrated lecture, commemorating Faraday's work, delivered in 1881. In 1874 Johnstone Stoney gave a clear statement of the atomic theory of electricity, and in 1891 he suggested the term "electron" to designate the "natural unit of electricity," which is that quantity of electricity which must pass through a solution to liberate at one of the electrodes one atom of hydrogen or one atom of any equivalent substance. He even estimated the amount of the charge as 3×10^{-11} absolute electrostatic units of quantity. This is a somewhat smaller value than that now accepted,

$$e = 4.774 \times 10^{-10} \text{ E.S.U.*}$$

Johnstone Stoney wrote : "A charge of this amount is associated in the chemical atom with each bond. There may accordingly be several such charges in one chemical atom, and there appear to be at least two in each atom. These charges, which it will be convenient to call 'electrons,' cannot be removed from the atom, but they become disguised when atoms chemically unite. If an electron be lodged at the point P of the molecule which undergoes the motion described in the last chapter, the revolution of this charge will cause an electromagnetic undulation in the surrounding ether." †

* See Millikan, *The Electron* (University of Chicago Press, 1924).

† Johnstone Stoney, *Sci. Trans. Roy. Dublin Soc.*, vol. 4, p. 563, 1891.

It is to be noticed that the term "electron" is here used for the elementary quantity of electricity, whether that quantity be positive or negative in sign.

Convincing evidence in favour of the existence of such "electric atoms" has been accumulating within the past quarter of a century, largely as the outcome of the experiments of Sir Joseph Thomson and his fellow workers at the Cavendish Laboratory at Cambridge. The charge carried by the negative electron, or "corpuscle" to use Thomson's term, is now known with considerable accuracy, and its mass has been found to be about $\frac{1}{1836}$ of the mass of the positive electron or "proton," the name given by Sir Ernest Rutherford to the nucleus of the hydrogen atom.

It is unnecessary to recount here the experimental methods that have been employed in determining the electron charge. For these reference may be made to Sir Joseph Thomson's *Conduction of Electricity through Gases* or to Professor Millikan's interesting book on *The Electron*. Nor is it needful to describe the development of the electron theory of matter, according to which material bodies are built up of atoms, each of which is an electrical system composed, according to Rutherford's theory, of a minute but massive nucleus (itself built up of electrons and protons) surrounded by the necessary number of negative electrons to give a neutral system. These subjects have been discussed by many writers, sometimes in a popular fashion, sometimes in a severely technical way. Mention may be made of Professor Andrade's book, *The Structure of the Atom*.

2. Faraday Tubes of Electric Force

The processes occurring in the electric field can be expressed by means of the conception, introduced by Faraday, of tubes of electric force, or rather of electrostatic induction. He showed that static electric induction took place in curved lines, a result which he regarded as incompatible with action at a distance, but in favour of his view of the action of contiguous particles of the dielectric (1166).^{*} Although he usually regarded the lines of force as chains of polarized particles, he seems to have realized that these lines of inductive action may stretch across a perfect vacuum (1616). This is the view adopted by Sir Joseph Thomson † who regarded the Faraday tubes as having their seat in the æther, the polarization of the particles which accompanies their passage through a dielectric being a secondary phenomenon.

^{*} Faraday, *Experimental Researches in Electricity*.

† *Recent Researches in Electricity and Magnetism*, Chap. I, 1893.

"In addition to the tubes which stretch from positive to negative electricity, we suppose that there are, in the æther, multitudes of tubes of similar constitution but which form discrete closed curves instead of having free ends; we shall call such tubes 'closed' tubes. The difference between the two kinds of tubes is similar to that between a vortex filament with its ends on the free surface of a liquid and one forming a closed vortex ring inside it. These closed tubes which are supposed to be present in the æther, whether electric forces exist or not, impart a fibrous structure to the æther."

Sir Joseph Thomson has developed and applied in many directions the theory of moving tubes of force, but unlike Faraday he regarded magnetism as a secondary effect, ascribing magnetic fields not to the presence of magnetic tubes but to the motion of electric tubes. The conception of lines of electric force stretching from positive to negative charges presents certain difficulties which have often been discussed. There is, for example, the case where magnetic fields occur without any manifestation of electric force. In order to account for such fields it may be supposed that two sets of Faraday tubes exist, starting from positive and negative charges respectively. In a steady magnetic field the positive and negative tubes may be thought of as moving in opposite directions with equal velocities. Such difficulties have led many physicists to reject the idea of the discrete existence of electrostatic tubes, in spite of the fact that "they give a natural and simple explanation of the electrokinetic momentum in the æther" (Jeans).

In a later chapter we shall discuss Thomson's application of the hypothesis of Faraday tubes to the problem of accounting for ionization caused by radiation. He assumed that the energy travelling outwards with a wave of light instead of being spread uniformly over the wave-front, is concentrated in those regions where pulses are travelling along the lines of force. Thus the picture of a wave-front suggested would be a number of bright spots on a dark ground.

3. Theories of Magnetism

When we turn from *electricity* to *magnetism* we find that the theories are less definite and the models less clearly cut. Coulomb attempted to account for the phenomena of magnetization by the existence of two magnetic fluids.

The first approach to a molecular theory is due to Poisson, who supposed that magnetic materials contained small spheres which are conductors of the magnetic fluids, and that their

behaviour in a magnetic field is analogous to that of conducting spheres in an electric field.

The real founder of the molecular theory is Weber,* who assumed that the molecules of an electric substance are themselves permanent magnets. Clerk Maxwell has said: "We may think of every portion of the magnet as *polarized*; that is to say, every particle or elementary piece of the bar may be regarded as a separate magnet." "Magnetization is a phenomenon, not of large masses of iron, but of molecules; that is to say, of portions of the substance so small that we cannot by any mechanical method cut one of them in two, so as to obtain a north pole separate from a south pole." "There are strong reasons for believing that the act of magnetizing iron or steel does not consist in imparting magnetization to the molecules of which it is composed, but that these molecules are already magnetic, even in unmagnetized iron, and that the act of magnetization consists in turning the molecules so that their axes are either rendered all parallel to one direction, or at least are deflected towards that direction."

The second essential feature of the modern theory was also realized by Weber, as has been pointed out by W. Peddie.† In the words of Clerk Maxwell: "The molecules do not turn with their axes parallel to x (the direction of the magnetizing force), and this is because each molecule is acted on by a force tending to preserve it in its original direction, or because an equivalent effect is produced by the mutual action of the entire system of molecules." Weber postulated a simple expression for the magnitude of the internal field spoken of in the last clause, saying: "But this back-acting force, arising from the mutual actions of the molecules, must increase with the deflection and can be represented by $D \sin \phi$, where D denotes a constant magnitude which one can call the molecular directive force."

According to the hypothesis of Ampère, the magnetization of the molecule is due to an electric current circulating in some closed path within it. As these molecular currents must continue without diminution it is necessary to suppose that there is no resistance offered to the passage of the current. Ampère's theory was devised before the induction of currents was known. Weber extended the theory and explained the phenomenon of diamagnetism as due to currents induced in the molecules by a variation in the magnetic field. These "molecular magnets" are now frequently spoken of as the "Weber elements," a term which is preferable because the former term suggests that the molecular magnet corresponds to the chemical molecule, which

* Weber, "Theory of Magnetism," *Pogg. Ann.*, vol. 87, p. 167, 1852.

† W. Peddie, *Nature*, vol. 120, p. 80, 1927.

is obviously not the case. In the older theories of paramagnetism the Weber elements were supposed to turn under the influence of the applied field so as to set their axes in the direction of the field, and this tendency was supposed to be resisted by forces of a quasi-elastic nature. Weber also introduced forces of a frictional character to enable him to account for ferromagnetic effects.

It is not a little remarkable that in papers written in 1871 Wilhelm Weber pictured the hypothetical molecular current, which Ampère had imagined to be continually flowing inside molecules, as the rotation of light positive charges about heavy negative ones. He wrote as follows: "The relation of the two particles as regards their motions is determined by the ratio of their masses e and e' , on the assumption that in e and e' are included the masses of the ponderable atoms which are attached to the electrical atoms. Let e be the positive electrical particle; let the negative be exactly equal and opposite, and therefore denoted by $-e$ (instead of e'). But let a ponderable atom be attracted to the latter so that its mass is thereby so greatly increased as to make the mass of the positive particle vanishingly small in comparison. The particle $-e$ may then be thought of as at rest, and the particle $+e$ as in motion about the particle $-e$. The two unlike particles in the condition described constitute, then, an Ampèrian molecular current."

Weber's model is identical with that assumed in the modern electron theory save in the fact that it is now the negative particle whose mass is negligible in comparison with that of the positive, so that the rôles of the particles are reversed. Langevin has developed this electronic theory of magnetism in which a negative electron circles in an orbit about a positively charged nucleus.

But to return to Weber's work on paramagnetism and ferromagnetism. Sir Alfred Ewing showed that Weber's assumption of frictional forces was unnecessary. He constructed models in which the controlling forces are magnetic only, and arise from the action of the neighbouring molecular magnets. This theory, put forward by Ewing in 1890, gave a qualitative explanation of the principal phenomena of ferromagnetism. It explained the three characteristic stages of magnetization as saturation is approached (Fig. 4).

In the first stage the intensity of magnetization, I , increases slowly and in proportion to the magnetizing field, H ; in the second stage the curve showing the relation between I and H is very steep, the value of I rising rapidly as H increases. After this the increase in I is slow, and eventually as magnetic saturation is approached I becomes nearly constant.

When the Weber elements are caused to turn by an applied

field there is first a small stable deflexion (this is the reversible stage), secondly a breaking-away from the position of stability through an unstable phase, and finally a settling down into a new position of stability. The theory also accounted for the main facts of magnetic hysteresis. Ewing* has recently pointed out that the old model fails quantitatively. Experiments show that the range of stable deflexion is very small. At the same time they show clearly that the control must be weak, for a small magnetizing force suffices to upset the equilibrium of most of the Weber elements. To account for the narrow limits of reversible deflexion it is necessary to suppose that the magnets are placed very close together; but this makes their stability

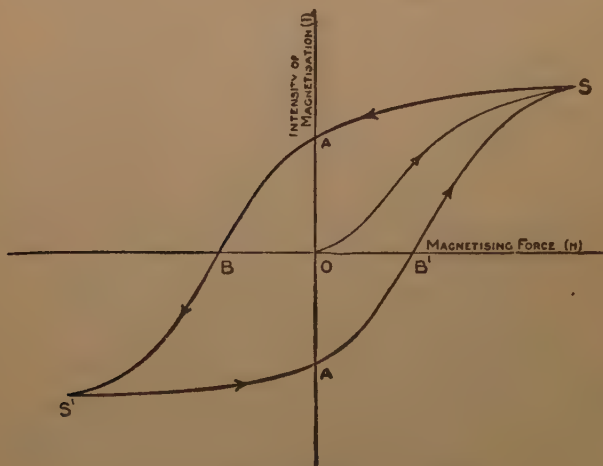


FIG. 4.—The Magnetic I-H Curve.

far too great—the field which would be required to change from the reversible to the irreversible stage is many thousands of times greater than that actually observed. To meet these difficulties Ewing has modified the original theory. In the new model a narrow range of stable deflexion is secured without excessive stability. This is obtained by so devising the model that the control of the Weber elements in each atom depends on the inequality between strong opposing forces. These forces are exerted separately on different parts of it by other constituents of the atom. The actual models devised by Ewing consisted partly of systems of small magnets, each magnet representing a Weber element, and partly of systems in which electric circuits

* J. A. Ewing, *Proc. Roy. Soc.*, vol. 100, p. 449, 1922; *Phil. Mag.*, vol. 43, p. 493, 1922.

played the part of the Weber elements, so as to correspond to the electron theory of the molecular magnet.

It is convenient to have a definite name for these Weber elements, and we may call them "magnetons," defining the word in the following way. The structure within the atom which behaves as the Weber element and may be regarded as the origin of tubes of magnetic induction, will be called a "magneton," using that term in its widest sense. This word seems to have been employed first by Dr. L. A. Bauer* in a paper read at a meeting of the Philosophical Society of Washington on 7th May, 1910. "The corpuscles in magnetism might be atomic systems in which the electron is revolving about an inner nucleus consisting, for example, of a positive ion. . . . Since the system creates an atomic magnetic field, the axis of which passes through the centre of rotation of the electron and perpendicular to the plane of rotation, the speaker suggests calling such systems 'magnetons.'"† The word was suggested and used independently about the same time by Professor Gans and by Professor Weiss, and is now well established in the subject.

Although the name "magneton" is of comparatively recent date the idea of a magneton has existed from at least the time of Weber's Works. In 1902 Voigt discussed magnetic elements consisting of homogeneous uniformly charged solids in rotation. In 1903 Abraham discussed a spherical electron in rotation and uniformly charged either over the surface or throughout the volume.

4. The Magneton of Weiss

Weiss gave the name "magneton" to the fundamental unit of magnetic moment which he believed he had discovered in the molecule of ferromagnetic substances. In the theory of magnetism it is often convenient to deal not with the magnetic moment per unit *volume* but with the magnetic moment per unit *mass*, and we may, if we choose, take as the unit of mass the gram atom. In this case the magnetic moment estimated for a single atom may be calculated if we divide the magnetic moment of the gram atom by Avogadro's constant, 6.062×10^{23} , the number of atoms in the gram atom.

Weiss carried out experiments first of all on the molecular susceptibility of magnetite. When this quantity was plotted against the reciprocal of the absolute temperature he obtained a series of straight lines, the slopes of these linear portions being in the ratio 4:5:6:8:10. This result Weiss attributed to a

* *Nature*, vol. 100, p. 227, 1917.

† *Science*, vol. 31, p. 920, June 10, 1910.

system of units,* and the current is due to a charge e making ν revolutions per second; hence $\phi = e\nu$. Assuming the orbit to be a circle of radius a , the area $A = \pi a^2$, and so we find

$$M_B = e\nu\pi a^2 \quad . \quad . \quad . \quad . \quad . \quad 3:2$$

But $2\pi\nu$ is the angular velocity ω , or the "pulsatance" in the orbit. Hence the magnetic moment of the Bohr magneton is given by

$$M_B = \frac{1}{2}ea^2\omega \quad . \quad . \quad . \quad . \quad . \quad 3:3$$

Now the moment of the momentum, or the angular momentum, or, as it is sometimes called, the "impulse moment," J , is equal to $ma^2\omega$. We notice that $a^2\omega$ occurs in both these expressions, and if we divide the magnetic moment by the angular momentum we obtain

$$\frac{M_B}{J} = \frac{1}{2} \frac{e}{m} \quad . \quad . \quad . \quad . \quad . \quad 3:4$$

According to the quantum hypothesis stated by Nicholson, the angular momentum J is equal to an integral multiple of $h/2\pi$, or

$$J = n \frac{h}{2\pi} (n = 1, 2, 3 \dots) \quad . \quad 3:5$$

When $n = 1$, i.e. for a one-quantum orbit, $J = h/2\pi$, and we have

$$M_B = \frac{1}{2} \frac{e}{m} \frac{h}{2\pi} = \frac{1}{4\pi} \frac{he}{m} \quad . \quad . \quad . \quad . \quad 3:6$$

as the magnetic moment of the Bohr magneton.

Substituting numerical values for h , e and m , we can calculate the moment of the one-quantum magneton, and we find that the Bohr magneton is 9.23×10^{-21} E.M.U. Multiplying by Avogadro's constant the magnetic moment comes out as $M_B = 5593$ E.M.U. per gram atom. This value is considerably larger than the magneton of Weiss, and it is certainly curious that the value of Bohr's magneton is almost exactly five times that of the Weiss magneton. This relation was first pointed out in 1914 by Chalmers † at the Birmingham meeting of the British Association. The relation had been noticed independently by Bohr himself and by others.‡ Taking the latest results for h and e/m it appears that there is a difference of something like 6 or 7 parts in 1000 between the two values.

There is no theoretical justification for the one unit being five times the other, but the author § has suggested one

* Many modern writers express the charge e in electrostatic units and the magnetic moment in electromagnetic units. In this case we must substitute e/c where e occurs in the text.

† See *Nature*, vol. 92, pp. 630, 687, 713 (1914).

‡ Richardson, *The Electron Theory of Matter*, p. 395 (1916).

§ H. S. Allen, *Phil. Mag.*, vol. 29, p. 718, 1915.

possibility in the way of explanation, taking the view that the magneton of Weiss might arise as a difference effect.

6. Other Suggestions as to the Magneton

A magneton of a somewhat different type was discussed by S. B. McLaren * in 1913, who put forward "a theory of magnets" in a short paper of great interest at the Birmingham Meeting of the British Association. In dealing with magnetism he emphasized the result, first proved by W. Voigt,† that strictly speaking, magnetic phenomena cannot be explained by the theory of the classical electron on the basis of the ordinary laws.‡ McLaren writes: "Even Langevin does not in reality offer any explanation of paramagnetism which goes deeper than Poisson's, where elementary magnets are already assumed. It is true that Langevin accounts for diamagnetism by resolving the elementary magnet into a swiftly circling electron. But when he comes to deal with paramagnetism he makes the fundamental assumption of all such theories. The electric current produces the same magnetic field as a certain magnetic doublet. Therefore, the reaction of an external field upon the current will produce the same effects as would be produced upon a permanent magnet. But indeed the assumption cannot be justified. This is clearly enough shown by one fact. The magnetic field acting upon a rotating electron can never do work, for the mechanical force is always directed at right angles to the electron's motion. But if the electric current is replaced by a magnet, and the magnet is assumed to place itself with axis parallel to the field, then certainly work is done. On the face of it there is here something which requires further investigation." Or putting it more strongly, "paramagnetism remains therefore a mystery."

McLaren formed the opinion that a theory of magnetism is possible, which succeeds where the electron theory fails. The electron theory makes matter the electric substance and relegates magnetism to a secondary place. "I suggest that matter is no more electric than magnetic substance; indeed, that matter has not in the last analysis the properties usually associated with substance at all. My hypothesis makes matter simply the boundary of the electromagnetic field." "It does not seem to me that a magnet can be identified with an electron in circular motion. To use modern language I suggest that the magneton

* An account of Professor McLaren's career and work, cut short by the War, is given in his "Scientific Papers," published as a memorial volume by the Syndics of the Cambridge University Press in 1925.

† W. Voigt, *Ann. d. Physik*, vol. 9, p. 115, 1902.

‡ S. B. McLaren, *Phil. Mag.*, vol. 25, pp. 48, 55, 1913.

ought to hold an equal place with the electron in our account of the nature of matter, neither is to be explained in terms of the other." "The electron and the magneton are merely internal boundaries of the electro-magnetic field. The concept of a field is already used by the electron theory and cannot be dispensed with."

McLaren assumed the electro-magnetic field to be defined by two vectors E and H , but the field does not occupy the whole of space—it is bounded by closed surfaces within which E and H do not exist. The space within these surfaces is "matter," the space without "æther." Over any such closed surface the electric induction is constant, and this constant defines the electric charge, which is yet not an electric substance. When the material surface is multiply-connected like an anchor ring, the magnetic induction across the aperture is constant, and the anchor ring may behave like a permanent magnet of constant moment.

Although these views were regarded as somewhat unorthodox, they were extremely suggestive, and may be looked upon as foreshadowing later work by others in which the ordinary classical conception of an electron has been somewhat roughly handled.

In 1915 the author* described an atomic model with a magnetic core, and the core of the atom in this model constituted a magneton, the magnetic moment arising from the rotation of positive or negative charges. In the same year an important paper was published by A. L. Parson,† bearing the title *A Magnetron Theory of the Structure of the Atom*. In this theory the magneton was looked upon as a thin, circular anchor ring of negative electricity rotating about its axis with large velocity (Fig. 5). Viewed from a point on its axis the ring appears as a circle, and the electricity is circulating round the ring, the electrical distribution being uniform. The point of difference between this and the earlier models lies in the fact that in the latter the electric charge is concentrated, while in this model the charge which is circulating round the ring is uniformly distributed. For this reason it is called the "ring electron." In a discussion held at a meeting of the Physical Society of London‡ in 1919 the case for and against such a ring electron was put forward. Although there are many arguments which may be adduced in favour of this conception, the prevailing feeling at the present time is rather against such an idea. The model, no doubt, is able to explain a considerable number of facts,

* H. S. Allen, *Phil. Mag.*, vol. 29, p. 714, 1915.

† A. L. Parson, *Smithsonian Miscellaneous Collections*, vol. 65, No. 11, 1915.

‡ *Proc. Phys. Soc.*, vol. 31, p. 49, 1919.

but any model that is to make a claim to uniqueness must meet the demands of all the different branches of Physics, and it does not seem as if the ring electron were able to satisfy these requirements. It may, however, be regarded as the forerunner of the modern "spinning electron." Another model which may also

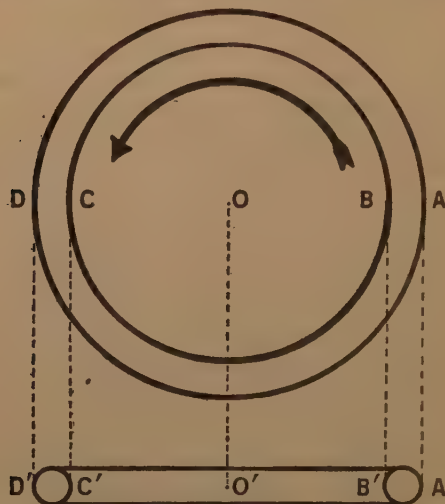


FIG. 5.—The Parson Magnetron or Ring Electron.

be described as a magneton is the mechanism imagined by E. T. Whittaker, suggested by Sir Alfred Ewing's models for the explanation of paramagnetic and ferromagnetic magnetization. This will be described in a later chapter. All these models fall under the definition of "magneton" which has already been given.

7. Quantum Magnetic Tubes

Planck's constant h may be regarded as a quantum of action. It is, however, for many purposes simpler to look upon this universal constant as an angular momentum. As already mentioned, J. W. Nicholson, in 1912, introduced the concept of a natural unit of angular momentum, finding such a unit in the quantity $h/2\pi$. This is the quantity which appears in Bohr's theory of the origin of spectral lines as the angular momentum of a "bound" electron.

Shortly before the European war S. B. McLaren was engaged in work on the properties of the magneton, and put forward in 1913 the important suggestion that the natural unit of angular

momentum postulated by Nicholson and Bohr might be identified with the angular momentum of the magneton. He regarded the magneton as an inner limiting surface of the æther, formed like an anchor ring. "The tubes of electric induction which terminate on its surface give it an electric charge, the magnetic tubes linked through its aperture make it a permanent magnet." For a magneton of any shape of cross-section the angular momentum, according to McLaren, is proportional to the product of the number of tubes of electric induction, N_e , and the number of tubes of magnetic induction, N_m . The proof of this important theorem was found amongst his papers after the war, and has been published (p. 54) in the memorial volume referred to previously.

In a paper published in the *Philosophical Magazine* in January, 1921, the writer gave a proof of the theorem for the

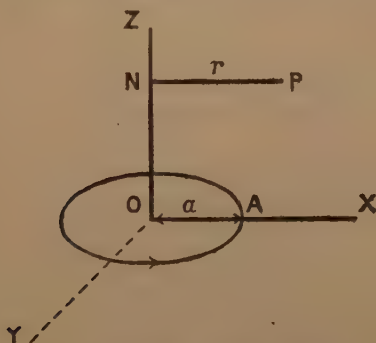


FIG. 6.—Field of a Ring Electron.

case of a ring electron in which an electric charge is rotating round the circumference of a thin anchor ring.

The charge which is rotating at a uniform rate carries with it tubes of electric polarization, and the motion of these tubes gives rise to a magnetic field. It was shown by J. J. Thomson * that when a tube of electric polarization is in motion there is a magnetic force produced equal to

$$H = 4\pi N_e v \sin\theta \quad . \quad . \quad . \quad . \quad . \quad 3:7$$

where N_e is the electric polarization, v the velocity of the tube, and θ is the angle between N_e and v . In the case we are considering $\theta = \pi/2$, so that $H = 4\pi N_e v$, consequently the magnetic energy per unit volume is

$$\frac{\mu H^2}{8\pi} = \frac{\mu 16\pi^2 N_e^2 v^2}{8\pi}$$

$$= 2\pi\mu N_e^2 v^2 \quad . \quad . \quad . \quad . \quad 3:8$$

* J. J. Thomson, *Recent Researches in Electricity and Magnetism*, § 12.

If we make the assumption that this magnetic energy may be interpreted as kinetic energy the equivalent mass per unit volume would be

$$\frac{1}{2}mv^2$$

where

$$\frac{1}{2}mv^2 = 2\pi\mu N_e^2 v^2 \quad . \quad . \quad . \quad . \quad . \quad 3:9$$

that is

$$m = 4\pi\mu N_e^2 \quad . \quad . \quad . \quad . \quad . \quad 3:10$$

The system, then, behaves as if there were in each unit volume a mass proportional to the square of N_e . Let the position of any point P (Fig. 6) in the electromagnetic field be referred to cylindrical co-ordinates, taking the axis of symmetry of the ring as the axis of z . Any element of volume at P at a distance r from the axis will have angular momentum of amount $mr^2\omega$, since $r\omega$ is the velocity of the element of volume. The angular momentum for unit volume is

$$4\pi\mu N_e^2 \times r^2\omega.$$

It will be convenient to denote this by A. The motion of the Faraday tubes produces a magnetic field in a direction at right angles to their length and to the direction of their motion, of magnitude

$$H = 4\pi N_e r\omega \quad . \quad . \quad . \quad . \quad . \quad 3:11$$

Thus

$$N_e = \frac{H}{4\pi r\omega} \quad . \quad . \quad . \quad . \quad . \quad 3:12$$

Hence the angular momentum for unit volume of the tube is

$$A = \frac{\mu H^2}{4\pi\omega} \quad . \quad . \quad . \quad . \quad . \quad 3:13$$

or more conveniently

$$A = \frac{2}{\omega} \times \frac{\mu H^2}{8\pi} \quad . \quad . \quad . \quad . \quad . \quad 3:14$$

Thus the total angular momentum associated with the ring electron is

$$\Sigma A = \Sigma \frac{2}{\omega} \times \frac{\mu H^2}{8\pi} \quad . \quad . \quad . \quad . \quad . \quad 3:15$$

taken over the whole field. But we know that $\sum \frac{\mu H^2}{8\pi}$ represents the whole magnetic energy associated with the magnetic field. It is easy to show that this may be written in the form

$$\frac{1}{2}Li^2$$

where L is the co-efficient of self-induction of the circuit and i is the current flowing round it. Thus the total angular

momentum is $\frac{Li^2}{\omega}$. The number of magnetic tubes linked with the circuit is by definition $Li = N_m$.

The total angular momentum is therefore given by

$$\Sigma A = N_m \times \frac{i}{\omega} \quad . \quad . \quad . \quad . \quad . \quad 3:16$$

where $\frac{i}{\omega}$, the current divided by the angular velocity, is equal to $e/2\pi = N_e/2\pi$ when we adopt the usual convention that each unit of charge is associated with one electrostatic tube.* So we obtain as the total angular momentum

$$\Sigma A = \frac{1}{2\pi} N_e N_m \quad . \quad . \quad . \quad . \quad . \quad 3:17$$

This result is quite independent of the quantum theory. It may be seen from a consideration of the dimensions of N_e and N_m that the product has the same dimensions as angular momentum. From the general nature of the proof it would seem that the same result would hold, not only for a line distribution of electrification, but also for a surface distribution or a volume distribution.

At this stage we introduce the quantum hypothesis in the form suggested by Professor Nicholson. Taking $h/2\pi$ as a natural unit of angular momentum we find for a ring electron in its simplest, or unitary condition the result

$$\frac{1}{2\pi} N_e N_m = h/2\pi \quad . \quad . \quad . \quad . \quad . \quad 3:18$$

leading to the striking identification

$$N_e N_m = h \quad . \quad . \quad . \quad . \quad . \quad 3:19$$

Or in words Planck's constant is equal to the product of the number of tubes of magnetic induction and the number of tubes of electric induction associated with this ring electron in its unitary condition. In the general case there may be n units of angular momentum giving us

$$\frac{1}{2\pi} N_e N_m = n \frac{h}{2\pi} \quad . \quad . \quad . \quad . \quad . \quad 3:20$$

$$\text{or} \quad N_e N_m = nh \quad . \quad . \quad . \quad . \quad . \quad 3:21$$

This value is consistent with the dynamical interpretation of

* Some writers define the lines of electrostatic force on the assumption that 4π lines are associated with unit charge. With this convention the results here given must be modified by introducing a factor 4π .

the quantum theory, for if the kinetic energy is represented by T ,

$$T = \frac{1}{2}Li^2 = \frac{1}{2}N_m \times i \quad . \quad . \quad . \quad 3:22$$

$$\text{and} \quad i = e\nu = N_e\nu \quad . \quad . \quad . \quad 3:23$$

where ν is the frequency. If we integrate for the complete period of the motion the quantum theory gives

$$\oint 2Tdt = nh \quad . \quad . \quad . \quad 3:24$$

$$\oint N_m N_e \nu dt = nh \quad . \quad . \quad . \quad 3:25$$

or, since N_m , N_e are constant,

$$N_m N_e \int \nu dt = nh \quad . \quad . \quad . \quad 3:26$$

$$N_m N_e = nh \quad . \quad . \quad . \quad 3:27$$

which is the same result as before. Probably the simplest way of interpreting this is to assume the existence of discrete tubes of magnetic induction, the unit tube being defined by

$$\frac{h}{e}.$$

If, instead of N_e we substitute the electron charge e , we get

$$N_m = n\left(\frac{h}{e}\right) \quad . \quad . \quad . \quad 3:28$$

The number of magnetic tubes is an integral number of times h/e . The unit magnetic tube is, then, determined by the ratio of Planck's constant, h , to the fundamental electron charge, e . Taking $h = 6.558 \times 10^{-27}$ erg sec.* and $e = 4.774 \times 10^{-10}$ E.S.U., we find that unit magnetic tube

$$= \frac{h}{e} = \frac{6.558 \times 10^{-27}}{4.774 \times 10^{-10}} = 1.374 \times 10^{-17} \text{ E.S.U.}$$

Assuming for the velocity of light the value $c = 2.999 \times 10^{10}$ cm./sec., we find in electromagnetic measure one unit magnetic tube equal to 4.120×10^{-7} C.G.S. This means that one C.G.S. "line of magnetic force" (one "Maxwell") contains 2.43×10^6 unit tubes, or "quantum tubes" as they might be termed.

The magnetic moment, M , for the system in its unitary state is found by multiplying the strength of the equivalent magnetic shell by the area, or multiplying the current by the area, and by the same method that was used for the Bohr magneton may be expressed as

$$M = \frac{he}{4\pi m}.$$

* Another value sometimes employed for h is 6.545×10^{-27} erg sec., the unit tube of magnetic induction is then 1.371×10^{-17} E.S. units or 4.113×10^{-7} E.M. units.

For the sake of simplicity and clearness in exposition we have confined our attention to the magneton in the form of a ring electron, but it must be remembered that McLaren's theorem as to tubes of magnetic induction is true for any magneton of the type which he considered.

There is a strong presumption that things which can be counted must have a physical existence, so we are led to regard these discrete quantum tubes of magnetic induction as physical realities. It is not necessary to discuss the significance we must attach to the word "reality," we may safeguard ourselves by speaking of "physical realities."

In view of the fact that one C.G.S. magnetic tube is a bundle containing about two and a half million quantum tubes, it is scarcely surprising that the smaller tubes have not revealed their existence as such in ordinary magnetic experiments. There is, after all, nothing novel in the suggestion of the actual existence of magnetic lines of force. Students of Faraday's *Experimental Researches* will find in Vol. III that he insists again and again on this point of view. Starting from the consideration of such lines in the abstract "as expressing accurately the nature, condition, direction, and amount of the force in any given region either within or outside of the bar [magnet]," he passes on to the inquiry "of the possible and probable *physical existence* of such lines" (p. 438). If the existence of *curved* lines of magnetic force be conceded he argues that the physical nature of the lines must be granted also. "I cannot conceive curved lines without the conditions of a physical existence in that intermediate space" (p. 414). "Again and again the idea of an *electro-tonic* state has been forced on my mind; such a state would coincide and become identified with that which would then constitute the physical lines of magnetic force" (p. 420). The question of the existence of physical lines of force he regards as "both important, and likely to be answered ultimately in the affirmative" (p. 437). Again, in the celebrated letter published under the title "Thoughts on Ray Vibrations" (p. 447) he writes: "The view which I am so bold as to put forth considers, therefore, radiation as a high species of vibration in the lines of force which are known to connect particles and also masses of matter together. It endeavours to dismiss the æther, but not the vibration." "It may be asked, what lines of force are there in nature which are fitted to convey such an action and supply for the vibrating theory the place of the æther?" "The lines of weight or gravitating force are, certainly, extensive enough to answer in this respect any demand made upon them by radiant phenomena; and so, probably, are the lines of magnetic force. . . ." These quotations are

sufficient to show Faraday's point of view, and as is well known, Clerk Maxwell developed and gave mathematical expression to these views. One of his earliest papers deals with the illustration of Faraday's lines of force by the lines of flow of a liquid (1856). Maxwell writes :

"In this outline of Faraday's electrical theories, as they appear from a mathematical point of view, I can do no more than simply state the mathematical methods by which I believe that electrical phenomena can be best comprehended and reduced to calculation, and my aim has been to present the mathematical ideas to the mind in an embodied form, as systems of lines or surfaces, and not as mere symbols, which neither convey the same ideas, nor readily adapt themselves to the phenomena to be explained."

By means of mechanical analogies, or as he says, dynamical illustrations, Maxwell sought to exhibit the phenomena of electricity and magnetism in a form in which the understanding can readily grasp them.*

We shall return in later chapters to the consideration of the relation of the quantum theory to the conception of tubes of electric or of magnetic induction.

* See an interesting article "On the Methods of Theoretical Physics," by Ludwig Boltzmann, *Proc. Phys. Soc.*, vol. 12, p. 336, 1893.

CHAPTER IV

LINE SPECTRA AND THE QUANTUM THEORY

The greatest achievement of all, and one to which we may reasonably look forward, has not yet been effected. No one has yet succeeded in tracing back from the periodicities, the intensities and other properties of the lines of a spectrum of an element what that motion of the electrons within the molecules must have been to have been able to produce just these precise effects. The information is given to us by nature in the spectrum exhibited to us. It is written there; but in a language which has never been deciphered.

G. JOHNSTONE STONEY (1906)

1. Series of Lines in Spectra

IN the classical experiment of Sir Isaac Newton (1666) a spectrum was formed on a screen by passing a beam of sunlight through a circular hole in a shutter and then through a glass prism. Although in some experiments he used a rectangular slit and a lens, it was not till 1802 that Wollaston, in the purer spectrum obtained by using a narrow slit, observed a number of black bands. Fraunhofer discovered the invariable position of these black lines in the spectrum, mapped their position and designated the principal lines by letters of the alphabet. He was the first to employ a sodium flame as a source of monochromatic light. Such light of one particular colour is now characterized by the wave-length (λ) or the frequency (ν) which determines the position in the spectrum. These two quantities are connected by the fundamental relation $c = \nu\lambda$ where c is the velocity of light.*

* Spectroscopists usually express the wave-length in terms of the Ångström Unit ($1 \text{ Å.U.} = 10^{-8} \text{ cm.}$) or the micro-millimetre ($1 \mu\mu = 10^{-7} \text{ cm.}$). Assuming the velocity of light to be $3 \times 10^{10} \text{ cm. per sec.}$ in free space, the frequency, ν (the number of complete vibrations executed in one second), is given by $3 \times 10^{18}/\lambda$ in Ångströms.

The unit of wave-length defined by the red cadmium line, $\lambda = 6438.4696$, has been called the International Angstrom (I.A.).

In the spectroscopy of Röntgen rays a smaller unit is employed called the X-Unit (X.U.) ($1 \text{ X.U.} = 10^{-12} \text{ cm.}$). This unit is only one thousandth part of the optical spectroscopic unit (1 Å.U.). Measurements of wave-lengths of X-rays depend on the distance between the lattice planes of some chosen crystal. The crystals in most frequent use are rock salt

It has long been known that certain spectra contain a definite series of lines, one of the most striking of the series being that found in the spectrum of hydrogen. A number of lines may be seen in the spectrum starting with a prominent red line coincident with the line observed by Fraunhofer in the solar spectrum and called the *c* line of hydrogen. In the solar spectrum this occurs as a dark line, in the emission spectrum of hydrogen as a bright line generally known as H_α . Other bright lines occur in the green, in the blue, or in the ultra-violet, and the series is indicated by the letters of the Greek alphabet $H_\alpha, H_\beta, H_\gamma \dots$. The spectrum is shown in Fig. 7 and it will be noticed that in passing towards the violet end of the spectrum the lines come closer together.

Many attempts had been made to obtain a numerical relation between wave-lengths of these lines, but the first that was completely successful was that made by Balmer in 1885. He found that the first nine lines of the elementary spectrum of hydrogen

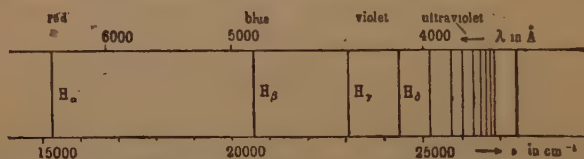


FIG. 7.—The Balmer Series in the Hydrogen Spectrum.

can be represented by a simple mathematical formula. The wave-length is given by

$$\lambda = 3645 \cdot 6 \frac{m^2}{m^2 - 4} \quad \dots \quad 4 : 1$$

where m is a positive integer to which we give in succession the values 3, 4, 5 . . . 11. Within the limits of error of observation this formula gives λ accurately. It was shown later that the same formula would account for the lines in the ultra-violet observed in the solar eclipse of 1898, as many as twenty-nine lines being measured. In modern work on spectra it is usually convenient to employ not the wave-length but the wave number. The number of complete waves in 1 cm. may be represented by N so that N is the reciprocal of λ , assuming that λ is expressed in centimetres.* We may now re-write Balmer's formula in terms of wave numbers, and put it in the form

$$N = N_R \left(\frac{1}{4} - \frac{1}{m^2} \right) \quad \dots \quad 4 : 2$$

and Iceland spar (calcite). The "initial" value $2.814 \times 10^8 \text{ cm.} = 2.814 \text{ Å.U.} = 2814 \text{ X.U.}$ is employed for rock salt, and the value $3.029 \times 10^8 \text{ cm.} = 3.029 \text{ Å.U.} = 3029 \text{ X.U.}$ is proposed for calcite.

* Or $N = 10^8 / (\lambda \text{ in Angström Units})$.

In this formula N_R is a constant known as Rydberg's constant, sometimes represented by a single letter R . If we take Rowland's scale of wave-lengths the value of this constant is 109675. Modern results are expressed on the International Scale, and according to Curtis * on this scale N_R for hydrogen has the value 109678.3. Birge † gives 109677.6 cm.⁻¹, a value differing from that of Curtis by less than 1 in 100,000. We may notice in passing the very great accuracy reached in determining these constants.

Balmer's formula may also be written in terms of the frequency of vibration, represented by ν , where if c is the velocity of light, $\nu = Nc$, $\nu_R = N_R c$. Consequently, as we have c on both sides of the equation, we can re-write it

$$\nu = \nu_R \left(\frac{1}{4} - \frac{1}{m^2} \right) \quad . \quad . \quad . \quad . \quad 4:3$$

Here ν_R is the fundamental Rydberg frequency, and the approximate value is 3.289×10^{15} sec.⁻¹. After Balmer's discovery many investigators turned their attention to this subject. In particular, Kayser and Runge made very accurate measurements of wave-lengths and tried to represent the wave number of a line in a spectral series by a mathematical formula. A most important step in advance was made by Rydberg in 1889, who showed that for other elements, most series can be represented approximately by a formula of the same type as that used by Balmer. Rydberg's formula, which is a modification of Balmer's, is:

$$N = N_R \left(\frac{1}{(m_0 + \mu_0)^2} - \frac{1}{(m + \mu)^2} \right) \quad . \quad . \quad . \quad . \quad 4:4$$

In this formula m_0 is usually 1; sometimes it may be equal to 2, as it is, for example, in Balmer's formula; or even to 3; m is a positive integer which takes a series of values which steadily increase for successive lines of the series. The quantities μ_0 and μ are small and are usually fractions less than 1. By means of such a formula it is possible to represent a great many series with fair accuracy. If we wish to obtain greater accuracy we may employ a more elaborate formula, and according to Rydberg such a formula should be written in the more general form

$$N = N_R \left(\frac{1}{D_0^2} - \frac{1}{D^2} \right) \quad . \quad . \quad . \quad . \quad 4:5$$

where the denominators may be more or less complicated expressions involving integers and fractions. For our purpose the

* Curtis, *Proc. Roy. Soc.*, vol. 96, p. 147, 1919.

† Birge, *Science*, vol. 64, p. 180, 1926.

simple form of Rydberg's formula will suffice, and we may conveniently re-write it as

$$N = \frac{N_R}{(m_0 + \mu_0)^2} - \frac{N_R}{(m + \mu)^2} \quad . \quad . \quad . \quad 4:6$$

It is important to notice that we have here the difference between two expressions, each of which is known technically as a "term." If we take such an expression as $\frac{N_R}{(m + \mu)^2}$ and substitute a series of integral values for m , we get a series of terms which form what is known as a "sequence." In any given spectral series, as, for example, Balmer's, the first term is regarded as a constant, and the series is obtained by giving a succession of integral values to m in the second or "current" term. It should be noticed that as this integer increases the lines of the series become closer and closer, and if m be made indefinitely great we should be left only with the first term, which represents the limit of the series, given by

$$N_\infty = \frac{N_R}{(m_0 + \mu_0)^2}.$$

The corresponding frequency is sometimes spoken of as the *convergence frequency*.

From the theoretical point of view, the great importance of Rydberg's work lies in the fact that the frequency is expressed as the difference between two terms. Such a result is very difficult to account for on the basis of classical mechanics. This was pointed out by the late Lord Rayleigh, who drew special attention to the fact that in this formula we have the frequency expressed in a form which we should not expect according to ordinary mechanical laws. As we shall see presently, the quantum theory does give us some account of these results, Bohr's theory being designed for this very purpose.

It is not always easy to identify a spectral series, but some assistance is given by the physical characteristics of the lines. Lines belonging to a particular series usually have the same properties, for example, all may be sharply defined or all may be nebulous. The intensity of the lines diminishes regularly as we pass from the longer to the shorter wave-lengths. One way of detecting a series is to look for the presence of doublets or triplets in the spectrum. A good illustration is afforded by sodium, of which the yellow D lines form the first members of a series of doublets. Another characteristic property that may be used is the behaviour of the lines in a magnetic field, first discovered by Zeeman (Chapter XV).

Apart from hydrogen there are four chief series which have

been recognized. Three of these were known to Rydberg and also to Runge, and the fourth was identified later by Bergmann. The first of these is generally called the *Principal Series* (P) which includes the strongest lines in the spectrum; the second is the *Diffuse Series* (D) which is composed of more nebulous lines of intermediate intensity; the third the *Sharp Series* (S), composed of sharply-defined lines weaker in intensity; and the fourth the *Fundamental* or *Bergmann Series* (F or B) which is found in the infra-red.

Each one of these series may be represented approximately by a formula of the Rydberg type. The limit of each series is given by an expression of the form $\frac{N_R}{(m_0 + \mu_0)^2}$, and we may represent the four limits conveniently as P_∞ , D_∞ , S_∞ , and F_∞ . Then the four series can be written down as follows:

(1) Principal Series $P(m) = P_\infty - \frac{N_R}{(m + P)^2}$, where m takes the values 1, 2, 3 . . .

(2) Diffuse Series $D(m) = D_\infty - \frac{N_R}{(m + D)^2}$, where m takes the values 2, 3, 4 . . .

(3) Sharp Series $S(m) = S_\infty - \frac{N_R}{(m + S)^2}$, where m takes the values 2, 3, 4 . . .

(4) Fundamental Series $F(m) = F_\infty - \frac{N_R}{(m + F)^2}$, where m takes the values 3, 4, 5 . . .

It is convenient to have a brief notation for the representation of series. Ritz, who has done a great deal of important work on the theory of spectral series, suggested that such a term as $\frac{N_R}{(m + \mu)^2}$ should be written simply as $m\mu$.

Rydberg and others have pointed out a number of important relations connecting these chief series. Using the abbreviated notation these relations can be expressed as follows:

$$\begin{array}{ll} P(m) = 1S - mP & m = 1, 2, 3 \dots \\ D(m) = 1P - mD & m = 2, 3, 4 \dots \\ S(m) = 1P - mS & m = 2, 3, 4 \dots \\ F(m) = 2D - mF & m = 3, 4, 5 \dots \end{array}$$

This is the notation in Fowler's *Report on Series in Line Spectra* (Physical Society of London, 1922), to which reference should be made for a more complete account of the subject.

2. The Theory of Ritz

All the relations which have been found between the lines of spectral series involve the frequency, and not the square of the frequency. This creates a difficulty in giving an explanation of the results on the basis of the classical theory, because, as Lord Rayleigh * pointed out, the laws of electric and elastic vibrations nearly always lead to an equation containing the square of the frequency. This is because the time enters in the form $\sin pt$, so that in finding the acceleration by a two-fold differentiation with respect to t , the factor p^2 is introduced. To meet this difficulty and so to account for the combination principle which he discovered, W. Ritz † at first examined the vibrations of an elastic membrane. He subsequently introduced a magnetic model, for in this case the forces acting depend, not on the position of a particle in the system, but on its velocity. In the model of Ritz the electron is supposed to describe a circular orbit in a magnetic field originating from two poles which occupy definite positions on the axis of the circle. A formula for the frequency is obtained which is analogous to Rydberg's, and, in particular, the Balmer lines of hydrogen can be obtained by assuming an appropriate number of elementary magnets placed end to end. The systems containing 1, 2, 3 . . . elementary magnets may be found either in *different* atoms of radiating hydrogen, or all these modifications may be imagined in one atom, or may succeed each other in time. It must be remarked that Ritz in his magnetic model employed an inverse square law, as did Bohr in the later electric model associated with his name.

3. The Quantum Theory of Line Spectra

We now turn to the quantum theory of Line Spectra, which is based by Niels Bohr (1913) on two groups of assumptions.

(1) "The atomic system can, and can only, exist permanently in a certain series of states known as *stationary states*. This series of states corresponds to a discontinuous series of values for the energy determined by the laws of classical mechanics in association with quantum relations. Any change of the energy of the system including emission and absorption of radiation must take place by a complete transition between two such states.

(2) "The radiation absorbed or emitted during a transition between two stationary states is mono-chromatic, having a definite frequency ν determined by the condition that $h\nu$ is equal

* Rayleigh, *Phil. Mag.*, vol. 44, p. 356, 1897.

† Ritz, *Ann. d. Physik*, vol. 25, p. 660, 1908.

to the difference between the values of the energy in the two states under consideration."

The above is a brief and formal statement of the assumptions made in the quantum theory of Bohr. The theory becomes clearer when we apply it to the particular case of the hydrogen atom. Adopting the model of the atom suggested by Rutherford, in hydrogen we have a single proton carrying unit positive charge and a single electron carrying unit negative charge. The mass of the proton is about 1800 times that of the electron. Approximately we may regard the proton as fixed and the electron as circling round it.

In the original form * of Bohr's theory it was assumed that the negative electron travelled in a circular orbit round a massive nucleus, the stationary states of the system being determined by Nicholson's postulate that the angular momentum is an integral multiple of $h/2\pi$. It will be convenient to summarize here the more important results thus obtained.

Consider, then, the case of an electron (charge e , mass m) moving in a circular orbit of radius a about a nucleus (charge E) situated at the centre of the circle (Fig. 3). The mass of the nucleus is assumed to be so large compared with that of the electron, that the nucleus may be regarded as fixed. The velocity v in the orbit is $a\omega$, where ω is the angular velocity; the acceleration is v^2/a towards the centre of the circle. The equation of motion of the electron may be written,

$$m \frac{v^2}{a} = mv\omega = ma\omega^2 = \frac{Ee}{a^2} \quad . \quad . \quad . \quad 4:7$$

as the only force in action is the electrostatic attraction between the charges. We get at once that

$$ma^3\omega^2 = Ee \quad . \quad . \quad . \quad 4:8$$

This equation is not in itself sufficient to specify the motion completely. There are two independent variables, a and ω , but only one equation of motion. According to the classical theory a and ω may vary continuously, and in fact owing to the dissipation of energy by radiation a would continually diminish and ω would continually increase. The electron after describing a spiral path would ultimately coalesce with the nucleus. As the orbit became smaller and smaller the rate of revolution would increase, and any radiation emitted would vary in frequency. The production of a line spectrum would be impossible.

But Bohr now introduces the quantum relation which limits the angular momentum, p , to integral multiples of $h/2\pi$. So we have

$$p = mav = ma^2\omega = nh/2\pi \quad . \quad . \quad 4:9$$

* *Phil. Mag.*, vol. 26, pp. 1, 476, 1913.

where n is a positive integer. Combining this with equation 4:8 we find that

$$v = a\omega = \frac{2\pi Ee}{nh} \quad . \quad . \quad . \quad . \quad . \quad 4:10$$

so that the velocity in the orbit becomes definite, and has a series of values determined by this relation. Substituting this value for v in the previous equations we obtain the value of a and of ω

$$a = \frac{n^2 h^2}{4\pi m E e}, \quad \omega = \frac{8\pi^3 m E^2 e^2}{n^3 h^3} \quad . \quad . \quad . \quad . \quad . \quad 4:11$$

Thus we see that the quantum relation restricts the circular orbits and the corresponding velocities to certain particular ones, which are "allowed" or "permitted" by the quantum relation. When moving in such an orbit the atomic system, composed of nucleus and electron, is said to be in one of its "stationary" states of motion, and it must be emphasized that in any such stationary state Maxwellian principles are suspended in the sense that no electromagnetic energy is radiated even though the motion of the electron is not uniform motion in a straight line.

The circular orbits which are permitted by the quantum theory are illustrated in Fig. 8, which shows the circles corresponding to $n = 1, 2, 3, 4$. Whilst the radius of the orbit is proportional to the square of the integer n the speed in the orbit is inversely proportional to n , and the periodic time ($2\pi/\omega$) is proportional to the cube of n .

In the case of the hydrogen atom $E = e$, and the radius of the innermost orbit, for which $n = 1$, is given by

$$a_1 = \frac{h^2}{4\pi^2 m e^2} = 0.531 \times 10^{-8} \text{ cm.}$$

It is often convenient to take the radius of this orbit as our unit of length. An electron moving round in this orbit represents the most stable condition of the hydrogen atom, but another orbit is possible in which the electron describes the circle marked by 2, the radius being four units; or again, a possible orbit is the circle marked by 3, the radius being nine units. Another circle, the fourth, has a radius of sixteen units. Here then we have a discontinuous series of orbits which may be represented by the numbers 1, 2, 3, 4, etc., numbering the orbits from the innermost away to infinity. The radius of an orbit is proportional to the square of one of the natural numbers, 1, 2, 3, 4 . . . Corresponding to each orbit a definite amount of energy would be associated with the atom, and the energy turns out to be

inversely proportional to the square of the radius. Thus the values for the energy are proportional to $1, \frac{1}{2^2}, \frac{1}{3^2}, \frac{1}{4^2} \dots$

When the hydrogen atom is neither emitting nor absorbing radiation the electron goes on circling in one or other of these so-called stationary orbits. But it sometimes happens that the electron jumps in some unexplained way from one orbit to another. When it does so, radiation is either emitted or absorbed. When the electron passes from a larger to a smaller orbit radia-

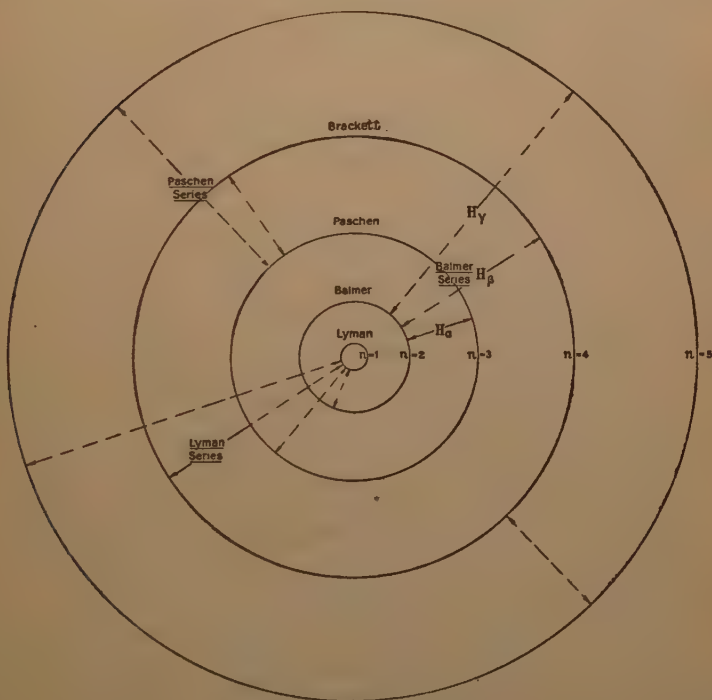


FIG. 8.—Circular Orbits.

tion is emitted—when it passes from a smaller to a larger one, radiation is absorbed. No suggestion is made in Bohr's theory as to what determines the transition, or as to how it happens. It is assumed that exactly one quantum of radiant energy is liberated from the atomic system in the process of emission, and this radiated energy passes away into space as absolutely monochromatic radiation. We may write the equation representing this fact :

$$h\nu = H_a - H_e \dots \dots \dots 4 : 12$$

where H_a represents the energy in the initial state, and H_e the energy in the final state of the atomic system.

Bohr's theory is not merely qualitative; it gives, as we proceed to show, a *quantitative* explanation of Balmer's series. The

velocity in the innermost orbit is $v_1 = \frac{2\pi e^2}{h} = 2.18 \times 10^8$ cm.

per sec. The ratio of this velocity to the velocity of light, c ,

is a pure number, and is given by $\frac{v_1}{c} = \frac{2\pi e^2}{hc} = a$. It is con-

venient to have a special symbol for this ratio: in a paper by the author,* it was denoted by q , but it is usually represented in Sommerfeld's notation by a . It is often useful to express the quantities with which we have to deal in terms of this constant number a . In the general case where the nucleus carries a charge $E = Ze$, we find that the expression for the velocity, v_n , in the orbit of quantum number n is

$$v_n = \frac{2\pi Ee}{nh} = \frac{Z}{n} ac \quad . \quad . \quad . \quad . \quad 4:13$$

Thus we have the velocity expressed in terms of the velocity of light.

We must now consider the energy of the atomic system in one of its stationary states. The energy is partly kinetic, T , and partly potential, V .

The kinetic energy

$$T = \frac{1}{2}mv^2 = \frac{2\pi^2 m E^2 e^2}{n^2 h^2} \quad . \quad . \quad . \quad . \quad 4:14$$

The potential energy

$$V = \frac{-Ee}{a} = \frac{-4\pi^2 m E^2 e^2}{n^2 h^2} \quad . \quad . \quad . \quad . \quad 4:15$$

The potential energy is numerically twice as great as the kinetic energy. The negative sign in the expression for the potential energy arises from the fact that the force is one of attraction. When the electron is brought nearer to the nucleus we gain a certain amount of energy, or have to expend negative energy. It will be noticed that $T = -\frac{1}{2}V$, a relation which, as Bohr † and Sommerfeld ‡ point out, is of very general application when the law of force is that of the inverse square of the distance.

* H. S. Allen, *Proc. Phys. Soc.*, vol. 27, p. 425, 1915.

† Bohr, *Phil. Mag.*, vol. 26, p. 24, 1913.

‡ Sommerfeld, *Atombau*, p. 475. The relation holds for orbits of any form provided the time average of the energy is considered in each case.

If H denotes the total energy (which is, of course, constant in the orbit),

$$H = T + V = -\frac{2\pi^2 m E^2 e^2}{n^2 h^2} \quad . \quad . \quad . \quad 4:16$$

Or putting $W = -H$

$$W = \frac{2\pi^2 m E^2 e^2}{n^2 h^2} \quad . \quad . \quad . \quad . \quad 4:17$$

This quantity W measures the work which must be done to move the electron from its orbit and carry it to a position of rest at an infinitely great distance from the nucleus.

Emission of radiation takes place, according to Bohr, when an electron jumps from an initial stationary orbit, defined by the quantum number n_a , to a final stationary orbit, defined by a smaller quantum number n_e . The frequency of the radiation emitted is determined by the condition

$$\begin{aligned} h\nu &= H_a - H_e \\ &= W_e - W_a \\ &= \frac{2\pi^2 m E^2 e^2}{n_e^2 h^2} - \frac{2\pi^2 m E^2 e^2}{n_a^2 h^2} \\ &= \frac{2\pi^2 m E^2 e^2}{h^2} \left(\frac{1}{n_e^2} - \frac{1}{n_a^2} \right) \quad . \quad . \quad . \quad 4:18 \end{aligned}$$

Dividing both sides of this equation by h , we find for the frequency

$$\nu = \frac{2\pi^2 m E^2 e^2}{h^3} \left(\frac{1}{n_e^2} - \frac{1}{n_a^2} \right) \quad . \quad . \quad . \quad 4:19$$

In the case of hydrogen the central charge E is numerically equal to e , and if, for convenience, we put

$$\nu_\infty = \frac{2\pi^2 m e^4}{h^3} \quad . \quad . \quad . \quad . \quad 4:20$$

we find that the frequency of a spectral line is given by

$$\nu = \nu_\infty \left(\frac{1}{n_e^2} - \frac{1}{n_a^2} \right) \quad . \quad . \quad . \quad . \quad 4:21$$

If we prefer to use wave-numbers instead of frequencies, we have

$$N = N_\infty \left(\frac{1}{n_e^2} - \frac{1}{n_a^2} \right) \quad . \quad . \quad . \quad . \quad 4:22$$

where
$$N_\infty = \frac{2\pi^2 m e^4}{h^3 c} \quad . \quad . \quad . \quad . \quad 4:23$$

This formula is of the type required for the explanation of Balmer's series, and, moreover, it gives very nearly the correct

value for the constant of Rydberg. When we substitute for the fundamental constants their known numerical values :

$$\begin{aligned}e &= 4.774 \times 10^{-10} \text{ E.S.U.} \\m &= 9.04 \times 10^{-28} \text{ gm.} \\h &= 6.558 \times 10^{-27} \text{ erg sec.}\end{aligned}$$

we obtain as the value of the Rydberg frequency 3.286×10^{15} sec.⁻¹, while the value of the Rydberg frequency for hydrogen from spectroscopic data is 3.2888×10^{15} sec.⁻¹. There is thus close agreement between the observed and the calculated values, a result which constitutes the first triumph of Bohr's theory.

The agreement, however, is not quite so close as the figures suggest, for we have neglected altogether the motion of the nucleus. In consequence of the relative motion of the nucleus * the value of Rydberg's constant, as given by the simple theory, is reduced in the ratio $\left(1 + \frac{m}{M}\right) : 1$, where M is the mass of the nucleus. For hydrogen the constant has its smallest value, which is given by

$$\nu_H = \frac{\nu_\infty}{1 + \frac{m}{M_H}} \quad \text{or} \quad N_H = \frac{N_\infty}{1 + \frac{m}{M_H}} \quad . \quad . \quad 4:24$$

The value 3.286×10^{15} sec.⁻¹ calculated from the basic constants should correspond to ν_∞ for which the experimental value is 3.2906×10^{15} sec.⁻¹. The small discrepancy is probably due to slight errors in the adopted values of the basic constants. We shall return to this point in Chapter XIV.

The lines in Balmer's series arise when the final orbit is determined by $n_s = 2$; this we may call orbit 2. The wave-number is given (in the notation of § 1) by

$$N = N_H \left(\frac{1}{2^2} - \frac{1}{m^2} \right) \quad . \quad . \quad . \quad 4:25$$

where $m = n_a = 3, 4, 5 \dots$

The line H_α is emitted when the electron transition takes place from orbit 3 to orbit 2. The line H_β is emitted when the electron jumps from orbit 4 to orbit 2, and H_γ when it jumps from orbit 5 to orbit 2 (see Fig. 8). We thus get a series of jumps or "switches," each jump corresponding to a particular line in Balmer's series.

Why should we make the electron finish up in orbit 2? Why should it not jump to orbit 1? This transition was proposed by Bohr himself and he suggested that there might be another series of lines represented by the formula $N = N_H \left(\frac{1}{1^2} - \frac{1}{m^2} \right)$.

* Sommerfeld, *Atomic Structure and Spectral Lines*, p. 218 *et seq.*

If we calculate the positions of these different lines we find that they all lie in the ultra-violet. This series had already been predicted by Ritz* and the first line at λ 1216 had been observed by Lyman.† Shortly after the publication of Bohr's paper other members were discovered by Lyman in the extreme ultra-violet spectrum of hydrogen.

If the electron finishes its jump in orbit 3, the series is given by $N = N_H \left(\frac{1}{3^2} - \frac{1}{m^2} \right)$, which is exactly the series observed by Paschen in the infra-red. Other lines were discovered by Brackett which correspond to the fourth circle being the final orbit of the electron. In this way then, Bohr provides a method of representing these spectral series in terms of quantum jumps. We do not get a real "explanation" of spectral series because we do not know what the jumps mean, no suggestion being made as to the nature of the transition.

It is not necessary to consider in detail the application of Bohr's theory to ionized helium. It will be sufficient to point out that in this case the nuclear charge is $2e$, and accordingly the value of Rydberg's constant, which depends on E^2 , will be four times the normal value. A correction will be required when the mass of the moving nucleus is taken into account.

The values of N for hydrogen and for helium are not exactly equal since M_H , the mass of a proton, is not the same as M_{He} , the mass of the helium nucleus. It can be shown that

$$\frac{N_{He}}{N_H} = \frac{1 + \frac{m}{M_H}}{1 + \frac{m}{M_{He}}} \quad . \quad . \quad . \quad . \quad 4:26$$

From this relation Fowler‡ calculated the ratio of the mass of an electron to that of a proton, and from a precise estimate of this kind Paschen§ obtained the result

$$M_H/m = 1843.7.$$

In the case of "stripped" atoms, from which all the extra-nuclear electrons save one have been removed, still larger values of Rydberg's constant will be required, the value of the constant being proportional to the square of the atomic number, Z . The value of N is practically the same for all but very light elements and is found to be $N_\infty = 109737.3$.

* Ritz, *Ann. d. Physik*, vol. 25, p. 667, 1908.

† Lyman, *Astrophys. Journ.*, vol. 19, p. 263, 1904; vol. 23, p. 181, 1906.

‡ Fowler, Royal Society, Bakerian Lecture, 1914.

§ Paschen, *Ann. d. Physik*, vol. 50, p. 935, 1916.

4. Energy Levels and Spectral Terms

The simple theory given by Bohr for the structure of the hydrogen atom forms a convenient introduction to the conception of "energy-levels" which plays such an important part in modern atomic theory. "An atom can stay for a very long time with its energy constant and equal to the value corresponding to one of these energy-levels, and during this period it emits no radiation. At intervals it may jump from one energy-level to another, and it is at these jumps only that energy is emitted or absorbed. A hydrogen atom losing energy must be compared, not to a ball rolling down-hill, but rather to a ball bouncing down a flight of steps" (Jeans).

Change may take place between any two of these levels and when the change occurs Bohr's frequency condition, $\pm h\nu = H_a - H_e$, must be obeyed. This fundamental frequency relation may be expressed by saying that in the change of an atomic system from an energy-level H_a to another energy-level H_e one quantum of monochromatic radiation $h\nu$ is either emitted or absorbed.

In the original presentation of Bohr's theory in which circular orbits alone were considered, a single quantum number n sufficed to determine the stationary states, and the corresponding energy values and moments of momentum. When elliptic orbits* were introduced by Wilson† and Sommerfeld,‡ and when Sommerfeld's theory of the fine structure of spectral lines was developed, two quantum numbers n and k were required, n being called the "principal" quantum number and k the "azimuthal" quantum number. In a simple ellipse n determines the semi-major axis and the energy value of the orbit, k determines the semi-minor axis, and is frequently written as a subscript to n , thus " n_k ."

The angular momentum of the electron is given by $\frac{kh}{2\pi}$. The eccentricity ε of the ellipse is determined by the equation $n^2(1 - \varepsilon^2) = k^2$. Thus when $n = k$, $\varepsilon = 0$ and the ellipse is a circle. When k is given in succession integral values less than n , the ellipses increase in eccentricity. The case $k = 0$ need not be considered here, as it corresponds to $\varepsilon = 1$, which would mean motion in a straight line through the nucleus.

It is instructive to consider the actual orbits corresponding to the smaller values of n .

* The results of the mathematical theory of quantized elliptic orbits are given in Appendix IV (p. 259).

† Wilson, *Phil. Mag.*, vol. 31, p. 161, 1916.

‡ Sommerfeld, *Ann. d. Physik*, vol. 51, pp. 1, 125, 1916.

As an illustration (see Fig. 9) when $n = 3$, there are three possible orbits, denoted by 3_3 , 3_2 , 3_1 . The first, 3_3 , is a circle identical with the third circular orbit of Bohr's simple theory; 3_2 is an ellipse of semi-minor axis $b = \frac{2}{3}a$; and 3_1 an ellipse of semi-minor axis $b = \frac{1}{3}a$. When $n = 2$, there are two possible orbits, a circular orbit 2_2 , and an ellipse 2_1 for which the minor axis is one half the major axis. When $n = 1$, the only possible orbit is the circular 1_1 orbit.

It has previously been stated that the energy is the same in all those orbits which have the same principal quantum number. This is true as a first approximation, but when we take into account corrections which have to be introduced in consequence

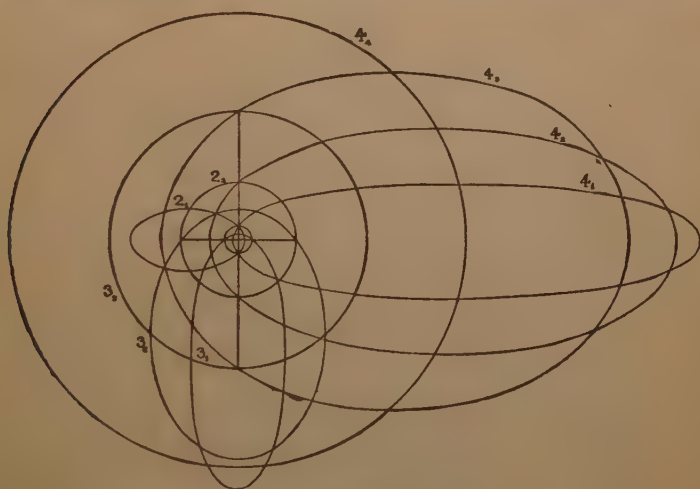


FIG. 9.—Elliptic Orbits.

No special significance attaches to the orientation of the orbits in the diagram.

of the variation of mass with speed, differences in energy arise in consequence of which the radiation emitted is not quite the same when the electron passes from the 3_3 to the 2_2 orbit, as when the electron jumps from the 3_2 or the 3_1 orbit, to the 2_2 or to the 2_1 orbit.

In Sommerfeld's treatment of the fine structure of the Balmer lines of hydrogen, taking into account the variation of mass with speed, there is superposed on the elliptic motion a slow rotation of the ellipse in its own plane about the nucleus. The path of the electron has, in consequence, the form of a rosette. The number k determines the period of rotation of the elliptic orbit in its own plane. The predictions of Sommerfeld's theory have received remarkable experimental verification in the work of

Paschen * on helium and in more recent investigations by others on hydrogen, but it should be mentioned that an alternative method of explaining the observations by means of a spinning electron is possible (Chapter XVII).

In the spectra of more complex atoms, somewhat similar results are found. The principal quantum number n determines the current number of the series term.† The azimuthal quantum number is the same for all terms of the same sequence. It appears that for the term type represented by S, $k = 1$; for P, $k = 2$; for D, $k = 3$. In addition there seems no reason why k should not be given larger values, and in fact for F, $k = 4$. In recent work the series have been extended; for G, $k = 5$; for H, $k = 6$, etc. Theoretically there is no limit to the number of types of terms.

In the case of sodium the well-known D line is a doublet, and forms the first member of a series composed of doublets. The spectra of the other alkalies have a similar doublet structure, while those of the alkaline earths have a triplet structure. In the latter there occurs also an independent singlet system.

When a spectral series is composed of doublets or triplets, a third quantum number is introduced (Sommerfeld, 1920) to distinguish individual components. This is called the "inner quantum number," and is now usually represented by j . It is commonly supposed that $j\hbar/2\pi$, which represents a certain amount of angular momentum, corresponds to the angular momentum of the entire atom. The inner quantum number is usually written as a subscript to the term symbol. Thus we may have the term P, the inner quantum number (e.g. 2) being written to the right and down below $P_{\frac{1}{2}}$.

The work carried out by Catalan ‡ at the Imperial College in London in 1922 has been of great importance in affording a clue to the structure of complex spectra. He discovered that in the spectra of manganese and of chromium there were terms of greater complexity than the triple terms which had previously been recognized. Thus in manganese the D terms had five values, corresponding to a quintet. The multiplicity of terms in spectra may vary from 1 up to 8 and may be either odd or even. In the more recent theories of Bohr, Sommerfeld and Landé a fourth quantum number, represented by r , has been introduced, which represents the *maximum multiplicity* of terms

* Paschen, *Ann. d. Physik*, vol. 50, p. 901, 1916.

† In Sommerfeld's work on elliptic orbits (1915) n occurs as the sum of the radial quantum number and the azimuthal quantum number. In every series the radial quantum number passes through all integral values from 0 to ∞ .

‡ Catalan, *Phil. Trans.*, vol. 223, p. 127, 1922.

in the system to which the term belongs. Thus $r = 1$ for singlets, 2 for doublets, 3 for triplets, etc. By general agreement r is written on the upper left of the term symbol. For example, 3P_1 represents a term of the triplet system for which $k = 2$ and $j = 1$.

Fowler, in his address to Section A of the British Association (1926), gives a table showing the values of the inner quantum number j corresponding to the various terms and systems.

INNER QUANTUM NUMBER

Odd Multiplicities

Terms	k	Singlets $r = 1$	Triplet $r = 3$	Quintet $r = 5$	Septet $r = 7$
S	1	0	1	2	3
P	2	1	0 1 2	1 2 3	2 3 4
D	3	2	1 2 3	0 1 2 3 4	1 2 3 4 5
F	4	3	2 3 4	1 2 3 4 5	0 1 2 3 4 5 6
G	5	4	3 4 5	2 3 4 5 6	1 2 3 4 5 6 7

Even Multiplicities

Terms	k	Doublet $r = 2$	Quartet $r = 4$	Sextet $r = 6$	Octet $r = 8$
S	1	1	2	3	4
P	2	1 2	1 2 3	2 3 4	3 4 5
D	3	2 3	1 2 3 4	1 2 3 4 5	2 3 4 5 6
F	4	3 4	2 3 4 5	1 2 3 4 5 6	1 2 3 4 5 6 7
G	5	4 5	3 4 5 6	2 3 4 5 6 7	1 2 3 4 5 6 7 8

It must be remarked that the values assigned to j are to a certain extent arbitrary, since only differences of values are actually employed in the combination rules. Sommerfeld, for example, assigns half-integral values to j in term systems of even multiplicity. This means that the values of j in the Table are to be reduced by one half for certain purposes.

In the earlier development of the subject of the fine structure of spectral lines inner quantum numbers could be assigned only in an arbitrary fashion so as to satisfy as far as possible the complicated experimental results. As the values assigned by Sommerfeld are frequently referred to in the literature of the subject, and are likely to be adopted, we reproduce his table showing how the j values are related to the values of the azimuthal number k and the multiplicity r .

VALUES OF j , the INNER QUANTUM NUMBER

Type of Term	$r \backslash k$	1	3	5	2	4
S	1	0	1	2	$\frac{1}{2}$	$\frac{3}{2}$
P	2	1	2 1 0	3 2 1	$\frac{3}{2}$ $\frac{1}{2}$	$\frac{5}{2}$ $\frac{3}{2}$ $\frac{1}{2}$
D	3	2	3 2 1	4 3 2 1 0	$\frac{5}{2}$ $\frac{3}{2}$ $\frac{1}{2}$	$\frac{7}{2}$ $\frac{5}{2}$ $\frac{3}{2}$ $\frac{1}{2}$

For example, in a triplet term, $r = 3$, of the D type ($k = 3$) the j values are integral, being 3, 2, and 1. For a doublet term, $r = 2$, of the P type ($k = 2$) the j values are half-integral, being $\frac{3}{2}$ and $\frac{1}{2}$.

DOUBLET SYSTEMS

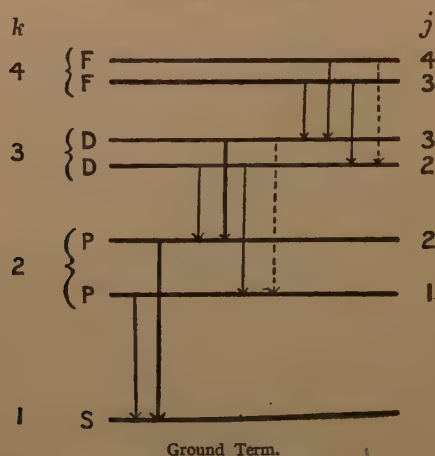


FIG. 10.—Energy Levels.

It is found that general rules may be formulated regulating the combinations of terms, although it must be remarked that exceptions to the rules are not infrequent. Fowler, in the address already mentioned, gives these selection rules as follows:

- (1) For different types of terms $\Delta k = \pm 1$.
- (2) For individual component terms $\Delta j = \pm 1$ or 0. (There is a further restriction imposed on j . The transition $j = 0, j = 0$ is forbidden, i.e. the inner quantum number cannot be zero in both of the two states concerned.)
- (3) For systems of terms $\Delta r = \pm 2$ or 0.

The results obtained by applying these rules may be represented in a convenient way by drawing horizontal lines to represent the energy levels (Fig. 10), and vertical arrows to show the transitions allowed by the selection rules.

In the Bohr model of the hydrogen atom the most stable

configuration, corresponding to the normal state of the atom, is that in which the electron is circling in the innermost or smallest orbit. The energy, H , of the atomic system then assumes its lowest value. Similarly in more complex atoms and ions there will be an energy level which represents the lowest value of the energy (or the term of highest numerical value). This deepest energy level, often referred to as the "ground term," is of special importance as it is related to the normal state of the atom. Systematic relations, as regards the ground term, have been discovered in passing from element to element through the periodic classification.*

From the theoretical point of view in which an atomic model is pictured, we may think of the atom as composed of a core and a series electron which may be supposed to orientate independently. Before the introduction of the spinning electron into the model this implied the consideration of two magnetic moments. In the simplest case, when the magnetic moments of the two constituents are in the same direction, the resultant moment of the atom was obtained by the addition of the two components. In general, however, these vectors will not be in the same direction, and Sommerfeld regarded j as being the resultant of the vector addition of j_s and j_a ,

$$(j = j_s + j_a),$$

the former, j_s , being due to the core, and the latter, j_a , to the series electron. He puts $j_s = \frac{1}{2}(\nu - 1)$ and $j_a = k - 1$.

This view, which led to grave difficulties of interpretation, is now superseded, and to mark the change in the meaning of the quantum numbers employed it is desirable to adopt the new notation employed by Sommerfeld.† In his later work j_s is denoted by s , a quantum number which receives its explanation by the introduction of the spinning electron. To every electron in its ground state there is assigned an amount of angular momentum $\frac{1}{2} \frac{h}{2\pi}$, so that for a single electron $s = \frac{1}{2}$.

When several valence-electrons are present, their momenta are compounded *algebraically*, giving $s = (\Sigma \pm \frac{1}{2})$. If the number of valence-electrons is even, s is an integer; if the number is odd, s is half an integer. As an example we may take the case of two outer electrons:

$$s = \frac{1}{2} + \frac{1}{2} = 1, \text{ Triplet system.}$$

$$s = \frac{1}{2} - \frac{1}{2} = 0, \text{ Singlet system.}$$

The multiplicity $\nu = 2s + 1$.

* See the Presidential Address of Prof. A. Fowler to Section A of the British Association, 1926.

† Sommerfeld, *Three Lectures in Atomic Physics*.

The quantum number j_a is now denoted by l , which is called the "group quantum number." This corresponds (for a single electron) to the angular momentum which is *added* when the series electron is excited, and its value in this case is $l = k - 1$. When there are several valence-electrons, the value of l is compounded *vectorially* from the several l 's. It is found that

for S	P	D	F	G	H
$l = 0$	1	2	3	4	5

The inner quantum number j is compounded vectorially from s and l .

Emphasis must be laid on the fact that spectroscopists have found it necessary to employ half-integral numbers in the explanation of their observations. This is marked in a most convincing way in band spectra. The simple theory would point to the levels of the vibration bands as being $n h \nu_0$ ($n = 0, 1, 2 \dots$), where ν_0 is the fundamental vibration frequency at infinitesimal amplitude. Here we use n to denote the vibration quantum number, not found in atomic spectra. In the band of boron oxide* the evidence is conclusive that the levels are $(n + \frac{1}{2}) h \nu_0$. In this case there can be no doubt, as the centre of the bands can be determined with certainty. As we shall see later, the new wave mechanics may be invoked to remove this difficulty.

We shall return to the question of spectral terms and the quantum numbers required for their specification in the next chapter, where it will be shown that there is an intimate connection between these terms and the possible states of an atom: that in fact atomic structure may be determined from spectroscopic evidence.

5. The Correspondence Principle

Bohr has always been careful to emphasize the contrast between the postulates of the quantum theory and the laws of the classical theory. Nevertheless, even in his earlier papers, he has pointed out that when the electron of the hydrogen atom is far removed from the nucleus, the frequency of the radiation emitted in a transition to a neighbouring orbit is very nearly the same as the frequency of the electron in its orbit. In the limit, i.e. in the region of large quantum numbers, there exists a *correspondence* between the frequency relations deduced by the two contrasted methods. Perhaps the simplest way of stating the Correspondence Principle is to say that the classical theory gives the right results in the limiting case when the action per

* Mulliken, *Phys. Rev.*, vol. 25, p. 259, 1925.

cycle of the system is large compared with Planck's constant, h , and in certain other special cases.

But Bohr has extended the scope of the Principle of Correspondence between the wave theory and the quantum theory, and has rendered it possible to obtain information as to the intensity and state of polarization of the emitted radiation from a consideration of the results of the classical theory. This has been done by correlating the various possible radiative processes with the harmonic vibration components which appear in the motion of the atom. To elucidate this correspondence we must remember that a compound oscillation may be analysed into its simple harmonic constituents by the method of Fourier. The motion of an electron in its orbit may be regarded as the resultant of a number of simple harmonic vibrations, the frequencies of which bear simple numerical relations to each other. Bohr assumes that every transition or quantum jump between two definite orbits corresponds to one and only one term of the Fourier series. It appears that a direct method can be found of setting up this one-to-one correspondence, so that we can "conjugate" each possible transition with a simple harmonic term. It must be remarked that the frequency of the radiation is *not* the frequency of the harmonic component, save in the limiting case of high quantum numbers. If a periodic term is missing in the classical theory it is assumed that the corresponding quantum transition does not take place.

The Correspondence Principle has been applied with great success, by Bohr* and Kramers and others, to the study of the Stark and Zeeman effects. It has been found possible to predict the state of polarization and the relative intensities of emission lines, the latter being a statistical problem depending on how frequently a certain event occurs in the atom. The Principle has also proved fruitful in fixing the stationary states, and there is no doubt that Sommerfeld is justified in calling it "a magic wand" which allows us immediately to make use of the results of the classical wave theory in the quantum theory.

By employing the principle of correspondence Bohr is enabled to throw some light on the applicability of the laws of conservation of energy and momentum to the processes of radiation.

"In the matter of method the principle of correspondence has the great advantage that it postulates that Maxwell's theory be generally valid for long waves (Hertzian vibrations of wireless telegraphy), and that it does not throw overboard the many useful results, which the classical theory gives for optical waves and Röntgen rays, but makes fundamental use of them. From this point of view the quantum theory seems, as Bohr has several

* Bohr, *Camb. Phil. Soc. Proc.* (Supplement), 1924.

times emphasized, not to deny the classical wave theory but systematically to extend it.

"We have to recognize the complete superiority of the principle of correspondence in the matter of atomic models. For here Bohr seems to have succeeded, by using classical mechanics and electrodynamics, in arriving at definite statements about the periodic system, which would have been inaccessible by any other route" (Sommerfeld, *Atomic Structure*, p. 276).

CHAPTER V

ATOMIC STRUCTURE AND COMPLEX SPECTRAL TERMS

One use of physical science is that it gives definite ideas.

SIR HUMPHRY DAVY

No fact discovered about the atom can be trivial, nor fail to accelerate the progress of physical science, for the greater part of natural philosophy is the outcome of the structure and mechanism of the atom.

SIR JOSEPH THOMSON: *The Romanes Lecture*, 1914

1. Atomic Numbers

THE *atomic weight* of an element long held an important position in physics and chemistry, but still greater importance must now be attached to the *atomic number*. This number may be defined as the integer which determines the position of the element in the periodic classification as established by Mendeléeff. The conception of such a number originated in 1862-3 in the work of de Chancourtois, and in that of Newlands in 1863-5. According to the former "the properties of the bodies (elements) are the properties of number." Newlands arranged the elements in the ascending order of their atomic weights, and proposed a "Law of Octaves," according to which: "The numbers of analogous elements, when not consecutive, differ by 7 or some multiple of 7." He admitted that it might be necessary to alter the number 7 to some higher figure, if other elements should be discovered. The chemical evidence for an atomic number has, in recent times, received overwhelming support from the physical side. Van den Broek first made the fruitful suggestion that the atomic number represents the number of negative electrons which constitute, along with an equal number of positive changes, an electrically neutral atom. This view was firmly established by the work of Moseley. His experiments on the X-ray spectra of the elements showed that there is a regular progression in the spectrum as we go from place to place in the periodic table, and that there is a definite integral number corresponding to each element, the integer

changing by unity in passing from one element to the next. The values determined in this way are, however, only relative. Moseley assumed that the characteristic integer for aluminium was 13, and based his results on this value. Evidence has accumulated that the choice made by Moseley was correct. Particular reference may be made to the work of Barkla on scattered X-rays. Barkla's experiments indicate 6 electrons for the atom of carbon, 7 for nitrogen, 8 for oxygen, 16 for sulphur and 1 only for hydrogen. These results may be collected in the form of a table.* (See opposite page.)

For the rare earths, which have not been included in this table, the atomic numbers are: La, 57; Ce, 58; Pr, 59; Nd, 60; Il, 61; Sm, 62; Eu, 63; Gd, 64; Tb, 65; Dy, 66; Ho, 67; Er, 68; Tm, 69; Yb, 70; Lu, 71.

The author has suggested the introduction of the term "molecular number" to signify the sum of the positive charges carried by the atomic nuclei contained in the molecule. Thus the molecular number bears the same relation to the atomic number as the molecular weight bears to the atomic weight. When a molecule contains a atoms of an element A, b atoms of B, and c atoms of C, its chemical formula may be written $A_aB_bC_c$, whilst its molecular number will be $N = aN_a + bN_b + cN_c$, where N_a , N_b , N_c are the atomic numbers of the component elements. For example, the molecular number of water (H_2O , hydrol) is 10, for the molecule contains two atoms of hydrogen (nuclear charge, 1) and one atom of oxygen (nuclear charge, 8). Thus the C.G.S. system of units is a decimal system in a deeper and more intimate sense than its originators supposed, for it is based on the assumption that the gram is the mass of 1 c.c. of water at the temperature at which its density is a maximum. This fact probably accounts for the remarkable numerical relations, involving powers of 10, which the author has shown to exist between certain fundamental physical constants.†

2. X-rays and Atomic Structure

From his investigations of the X-ray spectra of the elements Moseley ‡ concluded that every element from aluminium to gold is characterized by an integer Z , which determines its X-ray spectrum. The spectrum of an element can, therefore, in general, be predicted from the spectra of its neighbours.

* H. S. Allen, *Trans. Chem. Soc.*, vol. 113, p. 391, 1918.

† H. S. Allen, *Proc. Phys. Soc. London*, vol. 27, p. 425, 1915.

‡ Moseley, *Phil. Mag.*, vol. 26, p. 1024, 1913; vol. 27, p. 703, 1914.

PERIODIC SYSTEM OF THE ELEMENTS

O	I	II	III	IV	V	VI	VII	VIII
He 2	H 1	Be or Gl 4	B 5	C 6	N 7	O 8	F 9	
Ne 10	Li 3	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	
A* 18	Na 11	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26 Co* 27 Ni* 28
Kr 36	K* 19	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	
	Cu 29	Sr 38	Yt 39	Zr 40	Nb or Cb 41	Mo 42	Ma 43	Ru 44 Rh 45 Pd 46
Xe 54	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te* 52	I* 53	
	Cs 55	Ba 56	The Rare Earths 71	Ha 72	Ta 73	W 74	Re 75	Os 76 Ir 77 Pt 78
				Pb 82	Bi 83	Po 84	—85	
Rn or Nt 86	Au 79	Hg 80	Tl 81	Th 90	Ux 91	U 92		
	—87	Ra 88	Ac 89					

* Elements not placed in the order of the atomic weights.

Z electrons surrounding the positive nucleus may be divided into several groups, each group being characterized by the work which must be done to extract an electron of that group from the atom. This "work of extraction" determines the "level" of the group. The critical absorption frequencies correspond to the extraction of an electron from a particular level.

The law as stated by Moseley must now be regarded as superseded by an exact selection rule, based on quantum theory. One very remarkable feature in the graphs obtained is the occurrence of breaks in the curves due to the completion of inner shells.

The absorption co-efficient of an element varies with the wave-length of the X-radiation employed, and in general the co-efficient increases rapidly with an increase of wave-length. At certain particular wave-lengths, known as the critical absorption wave-lengths, sharp discontinuities appear, a sudden decrease in absorption taking place for a slight increase in the wave-length. In 1913 de Broglie obtained spectral photographs showing bands with sharp edges indicating a sudden change in absorption for a particular wave-length. The absorption discontinuity is directly explained by Bohr's theory.

It is found that the K series gives one absorption edge, the L series three, and the M series no less than five. We may conclude that there are three different energy levels within the L level, and five energy levels within the M level. Fig. 11 shows a scheme of energy levels based on these considerations, and some of the transitions corresponding to observed lines.

There is a striking analogy between optical spectra and X-ray spectra, the classification of the terms and the distribution of the lines being similar in the two cases. This resemblance has led to very interesting new ideas which will be taken up later.

For detailed discussions of X-ray spectra reference may be made to *X-Rays* by Maurice de Broglie (Methuen) or to *X-Rays and Electrons*, by A. H. Compton (Macmillan).

3. The Arrangement of the Electrons in Space

When we attempt to construct a model showing the spatial distribution of the electrons, it is necessary to make some hypothesis with regard to the distribution of the positive electricity of the atom. Lord Kelvin suggested that the atom might be regarded as a sphere of positive electricity in which negative electrons were distributed in definite configuration. Following this suggestion, J. J. Thomson made a famous attempt to explain

the periodic properties of the elements on the basis of the stability of such configurations. "Although Thomson's assumption regarding the distribution of the positive electricity in the atom is not consistent with more recent experimental evidence, nevertheless his work has exerted great influence upon the later developments of the atomic theory on account of the many original ideas which it contained" (Bohr).

The atomic model now generally accepted supposes that the resultant positive charge is concentrated in an extremely minute nucleus which is surrounded by the negative electrons. In 1904 Professor Nagaoka discussed an atomic model of this kind, which may be termed a saturnian atom. He imagined an attracting centre and a large number of equal particles repelling one another inversely as the square of the distance moving round the circumference of the circle. Very similar is the "nuclear atom" developed by Sir Ernest Rutherford in 1911. It is to Rutherford that we owe the experimental evidence in favour of this model, for he showed that the positive charge is concentrated in a nucleus of extremely small dimensions, containing practically the whole mass of the atom, whilst electrons are arranged round about the nucleus in certain orbits or in certain definite rings.

The theory developed by Bohr on the basis of the old quantum theory makes use of this atomic model, and a particular electron is supposed to describe an orbit which may be specified by one or more quantum numbers. Kossel on the one hand, and Lewis and Langmuir on the other, have emphasized the fact that in the periodic system there are certain elements which must correspond to especially stable configurations of electrons. These are the inactive gases helium, neon, argon, krypton, xenon and niton (radon).

TABLE OF ELECTRON CONFIGURATIONS

<i>Langmuir.</i>	<i>Element.</i>	<i>Bohr.</i>
2	Helium	
2 8	Neon	2 ₁ 8 ₂
2 8 8	Argon	2 ₁ 8 ₂ 8 ₃
2 8 8 18	Krypton	2 ₁ 8 ₂ 18 ₃ 8 ₄
2 8 8 18 18	Xenon	2 ₁ 8 ₂ 18 ₃ 18 ₄ 8 ₅
2 8 8 18 18 32	Niton	2 ₁ 8 ₂ 18 ₃ 32 ₄ 18 ₅ 8 ₆

The small subscript figures which appear on the right indicate the character of the orbit in Bohr's theory. It will be noticed

that whilst in Langmuir's theory the number of electrons in the outer shell increases up to 32, in Bohr's theory the outermost electrons never exceed eight in number.

If we think, for example, of the element neon with atomic number 10, this must have ten electrons arranged in some regular configuration of great stability. Fluorine, which has only nine electrons, must owe its electro-negative character to the fact that it has a tendency to capture an additional electron to make up the number ten, corresponding to maximum stability. The electro-positive character of sodium may be explained by supposing that one of the eleven electrons of sodium in the neutral atom is readily lost, a fact illustrated in the photo-electric activity of such an element.

Bohr attempted to solve the problem of finding the distribution of the electrons among various possible types of orbit. This he did by methods partly theoretical, partly empirical. In his theory of atomic structure emphasis is laid on the capture and binding of successive electrons by the positively charged nucleus. For an element of atomic number Z the process of formation of the neutral atom is supposed to occur in Z stages.

It has been found possible to divide the planetary electrons surrounding the nucleus into groups characterized by the total quantum number of the orbit. In the hydrogen atom, as we have seen, a large number of orbits are possible, some being circular, some elliptic. The most stable arrangement corresponding to the hydrogen atom in its normal state is that in which the single electron is bound in a circular orbit. The structure of the neutral helium atom is still somewhat uncertain, but the two electrons form a definite group called the K group. Formerly the two electrons were supposed to move in r_1 orbits in planes inclined to each other at an angle of 120° . Sommerfeld in 1923 suggested that they revolve in opposite senses in co-planar orbits.

Whatever may be the correct model, it must constitute a "closed" or "completed" (*abgeschlossenes*) configuration, characterized by $j = 0$. As the charge of the nucleus increases, this K group retains its characteristics, but the electrons move more rapidly and approach closer to the nucleus because of the more powerful electrostatic attraction. In lithium, the next element in the periodic table, when $Z = 3$, the third electron is bound in a 2_1 orbit. As we pass from helium to neon a new group of electrons is added which we may call the L group, characterized by the quantum number 2. The complete L group contains eight electrons as in neon. In all atoms of atomic number greater than 18 this L group appears. When it has been com-

pleted, a new group, the M group, begins to form outside it, and this kind of process continues throughout a series of elements, until, finally, we reach uranium.

It must be noticed that one or more of the electrons of one group may penetrate deeply into the region mainly occupied by another group. This occurs in an orbit of large eccentricity, or low azimuthal quantum number and is held to involve additional firmness of binding. It is by considerations of this kind that Bohr accounts for the occurrence and properties of what we call "transition" groups of elements. This is shown in a diagram due to Bohr, reproduced below.

1	H	3	Li	11	Na	19	K	37	Rb	55	Cs	87	-
2	He	4	Be	12	Mg	20	Ca	38	Sr	56	Ba	88	Ra
		5	B	13	Al	21	Sc	39	Y	57	La	89	Ac
		6	C	14	Si	22	Ti	40	Zr	58	Ce	90	Th
		7	N	15	P	23	V	41	Nb	59	Pr	91	Pa
		8	O	16	S	24	Cr	42	Mo	60	Nd	92	U
		9	F	17	Cl	25	Mn	43	-	61	-		
		10	Ne	18	Ar	26	Fe	44	Ru	62	Sm		
						27	Co	45	Rh	63	Eu		
						28	Ni	46	Pd	64	Gd		
						29	Cu	47	Ag	65	Tb		
						30	Zn	48	Cd	66	Dy		
						31	Ga	49	In	67	Ho		
						32	Ge	50	Sn	68	Er		
						33	As	51	Sb	69	Tm		
						34	Se	52	Te	70	Yb		
						35	Br	53	I	71	Lu		
						36	Kr	54	X	72	Hf		
										73	Ta		
										74	W		
										75	-		
										76	Os		
										77	Ir		
										78	Pt		
										79	Au		
										80	Hg		
										81	Tl		
										82	Pb		
										83	Bi		
										84	Po		
										85	-		
										86	Rn		

A Periodic Classification of the Elements (Bohr).

This form of periodic table was originally suggested by Julius Thomsen. The vertical columns here represent the periods. The presence of lines joining pairs of elements in successive vertical columns indicates that the pairs possess similar properties. One of the notable features of Bohr's classification is the success achieved "in accounting for the appearance, at certain stages, of elements which deviate in their properties from corresponding elements in the previous periods." By way of illustration let us consider more in detail the elements from argon to copper. In argon the K level is filled up with two electrons, the L level with eight electrons, but the M levels are not completely filled up by the eight electrons which occupy

the 3_1 and the 3_2 orbits. It might have been expected that in potassium the nineteenth electron would go into the 3_3 orbit, but owing to penetration a 4_1 orbit has stronger binding than a circular 3_3 orbit with no penetration. Consequently this additional electron is actually in an N level and not in an M level. In scandium, however, which has 21 electrons altogether, it appears that on account of the increased nuclear charge the nineteenth electron enters the 3_3 orbit. From scandium to nickel development occurs in the underlying M group. Consequently the frame encloses a group of elements in which development is taking place in an underlying level. When we go to copper, the normal development again sets in. In the fifth period of the periodic table from rubidium to xenon, we witness a similar "reorganization" of the N group in passing from yttrium, with atomic number 39, to palladium, with atomic number 46, corresponding to the completion of the normal 4_3 orbits.

In the sixth period two frames have had to be introduced, the inner one corresponding to a different type of reorganization in the completion of a 4-quanta level, and giving rise to the rare earths. Thus the primary division of the planetary electrons is into groups characterized by certain integers which determine the various levels:

$n = 1$	corresponding to the K level,			
$n = 2$	"	"	L	"
$n = 3$	"	"	M	"
$n = 4$	"	"	N	" etc.

But closer examination shows that these groups must be subdivided into smaller groups depending on subsidiary quantum numbers, and the later theories make use of two such subsidiary quantum numbers k and j . Here there occurs a difference in arrangement between the original scheme of Bohr and the later scheme proposed by Main Smith in the first instance on chemical grounds, and put forward independently by Stoner mainly from X-ray considerations. It is now admitted that this later arrangement is superior in several respects to the original scheme of Bohr, and in the subsequent work we shall employ this classification. Experiments show quite definitely that there is one K level, but there are three L levels, five N levels, and probably seven M levels. This is provided for in the modified scheme which is given on page 78.

The details of the scheme, as given by A. Fowler in his presidential address to Section A of the British Association of 1926, are shown in Appendix V.

ARRANGEMENT OF ELECTRONS IN RARE GASES
(Main Smith and Stoner)

	Atomic number	K I_{11}	L $2_{11} \ 2_{21} \ 2_{22}$	M $3_{11} \ 3_{21} \ 3_{22} \ 3_{32} \ 3_{33}$	N $4_{11} \ 4_{21} \ 4_{22} \dots$
He	2	2			
Ne	10	2	2 2 4		
A	18	2	2 2 4	2 2 4	
Kr	36	2	2 2 4	2 2 4 4 6	2 2 4
	n_k	I_1	$2_1 \ 2_2$	$3_1 \ 3_2 \ 3_3$	$4_1 \ 4_2$

In the light of Stoner's scheme of electron distribution, Sommerfeld has recently given the following table to show the classification of X-ray levels :

K	L_I	L_{II}	L_{III}	M_I	M_{II}	M_{III}	M_{IV}	M_V
K	L_{11}	L_{21}	L_{22}	M_{11}	M_{21}	M_{22}	M_{32}	M_{33}
1s	2s	$2p_1$	$2p_2$	3s	$3p_1$	$3p_2$	$3d_2$	$3d_3$
2	2	2	4	2	2	4	4	6

N_I	N_{II}	N_{III}	N_{IV}	N_V	N_{VI}	N_{VII}
N_{11}	N_{21}	N_{22}	N_{32}	N_{33}	N_{43}	N_{44}
$4s$	$4p_1$	$4p_2$	$4d_2$	$4d_3$	$4f_3$	$4f_4$
2	2	4	4	6	6	8

In the first line of the table is given the designation of the levels according to Bohr and Coster ; in the second line the nomenclature adopted by Sommerfeld in the new edition of his book, the double suffixes corresponding to the k and j of Landé ; the third line shows the correspondence throughout with the doublet character of the alkalis, the subscript index giving the inner quantum number j ; the last line gives the quantum weights of the respective terms as $2j$, which, according to Stoner, is equal to the number of electrons in the completed X-ray sub-groups.

4. Complex Spectra and their Interpretation

A great advance in our knowledge of atomic states and spectral terms has been brought about by the important researches of

Pauli,* Heisenberg,† and Hund.‡ Through their work “the foundations have been laid for the interpretation of spectra in terms of atomic states, and it appears that we can now predict, almost with certainty, the structure and chief characteristics of any optical spectrum of the atom of any element when the extra-nuclear electronic configuration that gives rise to it is known. Conversely, if the characteristics of any optical spectrum of an atom be known, it is possible likewise definitely to describe the extra-nuclear electronic states of the atom involved in the production of such spectrum.” §

The new theory arises out of the work of Russell and Saunders || on the spectra of the alkaline earths. Here we have to do with two outer electrons and it appears that the so-called “anomalous terms,” which had been discussed independently by Wentzel,¶ require for their theoretical explanation the resultant momentum of these electrons to be quantized. The corresponding quantum number, called the “group quantum number,” is denoted by l in Sommerfeld’s notation (instead of k used by Russell and Saunders).

Bohr has suggested that in elements like the alkaline earths, the two valency electrons may *both* be displaced to outer orbits. From a study of certain anomalous terms in the spectrum of calcium, Russell and Saunders concluded that it is possible for an atom to remain neutral while absorbing more energy than is required for the removal of the series electron. This may be explained, in accordance with a suggestion made earlier by Bohr, by supposing that “the energy must be divided between two (or more) electrons, each of which is displaced to a higher energy level, without the removal of either of them.” “The detailed numerical evidence led inevitably to the conclusion that both valency electrons might jump at the same time from outer to inner orbits, and that the net loss of energy would be then radiated as a single quantum, i.e. as monochromatic emission.”

There is here an extension of the earlier conception of Bohr as to the emission of monochromatic radiation constituting a

* Pauli, *Zeits. f. Physik*, vol. 31, p. 765, 1925.

† Heisenberg, *Zeits. f. Physik*, vol. 32, p. 841, 1925.

‡ Hund, *Zeits. f. Physik*, vol. 33, p. 345; vol. 34, p. 296, 1925.

§ McLennan, McLay, and Grayson Smith, *Proc. Roy. Soc.*, vol. 112, p. 76, 1926. A summary is given of the Heisenberg-Hund theory, and its application illustrated by examples. An outline of the scheme is also given in a paper by Fowler and Hartree, *Proc. Roy. Soc.*, vol. 111, p. 83, 1926.

|| Russell and Saunders, *Phys. Rev.*, vol. 22, p. 201, 1923; *Astrophys. Jour.*, vol. 61, p. 38, 1925.

¶ Wentzel, *Phys. Zeits.*, vol. 24, p. 106, 1923; vol. 25, p. 182, 1924.

single spectral line, because we must now take into consideration not only single electrons, but an atomic system comprising a considerable number of electrons. In this case the atom must be regarded, at least from one standpoint, as a complete and independent system. It may be remarked here that results of a similar character have been found in the formation of band spectra, the individual lines of which are now associated with changes in the energy of rotation and configuration of molecules. For further information on this important subject reference may be made to the Bulletin of the National Research Council (No. 57) on *Molecular Spectra in Gases* (1926).

In the theory of Heisenberg and Hund (published in 1925) five quantum numbers are used to specify an electron orbit, viz. n , k_1 , k_2 , m_1 , m_2 ; but of these five numbers only four are independent. The principal quantum number n retains the same meaning as in Bohr's central orbit theory. If k denotes, as is customary, the azimuthal quantum number, $k_1 = k - \frac{1}{2}$, and k_2 may be either $k_1 - \frac{1}{2}$ or $k_1 + \frac{1}{2}$, so that either $k_2 = k - 1$ or $k_2 = k$. Finally m_1 and m_2 are the magnetic quantum numbers for weak and strong fields respectively.

Three quantum numbers are required to specify a spectroscopic term, these are denoted by τ , l , and j , and may be identified respectively with the multiplicity, the group quantum number, and the inner quantum number referred to in the previous chapter.* The main object of the theory is to deduce the values of these term numbers, τ , l , j , from the quantum numbers of those electrons which are in uncompleted groups. This is done by employing a set of rules, partly theoretical, partly empirical, which serve to determine the possible states of the system.

Probably the most important principle limiting the number of possible electronic orbits is that enunciated by Pauli. It may be stated as follows: Four independent quantum numbers being required to determine uniquely an electronic orbit, two electrons cannot move in orbits characterized by exactly the same four quantum numbers. Thus there cannot be more than one electron in each uniquely defined quantum state, or in other words, there is only one possible electronic orbit of a given size, shape and position. It can be shown that this principle leads to the scheme of electron distribution proposed by Main Smith and by Stoner.

The actual procedure followed in determining the terms is somewhat lengthy, and for examples reference must be made

* As different conventions have been used for the absolute values to be assigned to the quantum numbers, some care is needed in dealing with the results of various authors.

to the papers already mentioned. It is necessary to consider the resultant action of all the electrons in uncompleted shells for the atom in question, and this may involve the consideration of numerous possibilities ; but the process is for the most part arithmetical and it may be said that the completion of the shells in the atom is decided "not by classical mechanics but by quantum arithmetic" (Sommerfeld).

These methods have met with brilliant success in the classification of spectra, even when the atom has more than two outer electrons. Hund* himself has investigated the iron group, and has predicted the electronic orbits in the rare earths. Bechert and Catalan† have examined the palladium group. R. H. Fowler and D. R. Hartree‡ have applied the theory to the spectrum of ionized oxygen (O II) and have found most satisfactory agreement between the terms deduced from the theory and those derived by A. Fowler from the analysis of the observed spectrum. McLennan§ and his fellow-workers in Toronto have investigated the structure of the spectrum of gold and of palladium.

Considerable importance attaches both in theory and in experiment to the so-called "raies ultimes" of de Gramont. Although not necessarily the strongest lines in the ordinary spectrum, these are lines which persist when the quantity of the element responsible for them is extraordinarily minute. Generally, these are supposed to be the resonance lines and the first members of principal series. This means that they correspond to transitions from the nearest possible orbit of higher energy to the lowest level or to the normal state of the atom. As a result of the Heisenberg-Hund theory it is now possible to predict the spectroscopic ground term associated with the normal state of each neutral atom, and also to specify with considerable confidence the actual electronic arrangement of all the elements. Tables exhibiting results of this kind have been given by Paul Foote,|| by McLennan McLay and Smith and by Fowler, in papers already cited. Fowler's Table is reproduced, by permission, in Appendix V, the values of the ground term directly determined from spectra being marked with an asterisk.

We may sum up the results of the more recent theories of atomic structure by saying that the character of a spectral term is determined by a set of quantum numbers which depend on

* Hund, *Zeits. f. Physik*, vol. 33, p. 345, 855, 1925.

† Bechert and Catalan, *Zeits. f. Physik*, vol. 35, p. 449, 1926.

‡ Fowler and Hartree, *Proc. Roy. Soc.*, vol. 111, p. 83, 1926.

§ McLennan, *Proc. Roy. Soc.*, vol. 112, pp. 76, 95, 110, 1926.

|| Paul Foote, *Trans. Amer. Inst. Mining and Metal Eng.*, No. 1547 D (1926).

the moments of momenta of all the electrons external to a completed shell. The simple character of the spectra of the alkali metals may be attributed to the fact that they each have but a single electron outside the completed shell which resembles that of the rare gases.

In concluding this necessarily brief account of the modern theory of the structure of the atom some reference must be made to the important work carried out by Saha.* He has investigated how the equilibrium distribution of the various "electronic isomers" depends upon temperature. (By electronic isomers are meant ions or atoms having the same nuclear charge and the same number of electrons.) This theory of high temperature ionization has been of great service in the interpretation of solar and stellar spectra. The first effect of increasing temperature will be to tear off the outermost electron from the atomic system, with the formation of the ionized atom which has lost one electron. This corresponds to what Lockyer called the "proto" element, the spectral lines being known as "enhanced" lines. The energy of ionization can be calculated from the ionization potential, or from the convergence frequency of the principal series, and the fraction of ionized atoms at a given temperature can be found by applying Saha's formula. The second stage in the process of ionization, in which the atom loses another electron, is then considered. The work of Saha corroborates the view of H. N. Russell that the continuous variation of stellar spectral types is mainly due to the varying values of the temperature of the stellar atmosphere.

* M. N. Saha, *Phil. Mag.*, vol. 40, pp. 472, 809, 1920; vol. 41, p. 267, 1921; *Proc. Roy. Soc.*, vol. 99, p. 135, 1921.

CHAPTER VI

QUANTIZATION IN SPACE

Another lesson that I learned by experience was that every progress in my thought was effected not by insisting upon the terms of the problems I had solved, but by the growth of new problems; and that these, though built upon the foundation of the old, were not their immediate consequence, but were excited by new impulses of feeling and new conditions of life.

BENEDETTO CROCE, *An Autobiography*

1. Theory of Spatial Quantization

A SURPRISING consequence of the quantum theory was deduced independently by Sommerfeld and Debye in 1916. In the absence of an external field or an internal atomic field, the orientation of an n_k orbit is indeterminate; but in the presence of such a field the orbit assumes a definite orientation with regard to the favoured direction provided by the field. Thus it becomes possible to specify not merely the size and form of the orbit, but also the position of the orbit in space, by means of quantum numbers. The orientation of the orbit is restricted to certain definite possibilities determined by the values of certain integral numbers. The experimental demonstration of such limited atomic orientations in a magnetic field was first suggested in 1921 by Stern, and we shall return later to the experimental work of Gerlach and Stern by which quantization in space was confirmed.

We consider first the *theory* of quantization in space. Let the line SN in the diagram (Fig. 12, page 84) represent the favoured direction determined by the lines of force, and let an electron be describing an orbit about the nucleus supposed to be at rest at O. A sphere of unit radius is drawn with O as centre, and KQ is the equator which determines the equatorial plane, OKQ. The line OP is supposed to point to the momentary position of the electron and the plane OKP, passing through A and B, is the orbital plane. As there are now three degrees of freedom, there are three quantum conditions and three quantum numbers are required to designate the particular orbit pursued by the

electron. The radial quantum condition along OP is the same as in the two-dimensional problem. It can be shown, as is done in Sommerfeld's book, *Atomic Structure and Spectral Lines*, p. 243, that the angular momentum in the plane of the orbit p_ϕ is equal to $k\frac{h}{2\pi}$, where ϕ is the "orbital azimuth" in this plane, and k is the "azimuthal" quantum number. The third quantum condition may be expressed by saying that the generalized momentum corresponding to the *resolved motion of the electron in the equatorial plane* is given by $p_\psi = m\frac{h}{2\pi}$, where m is a new quantum number which may be called the "equatorial" quantum number. It must be noticed that this

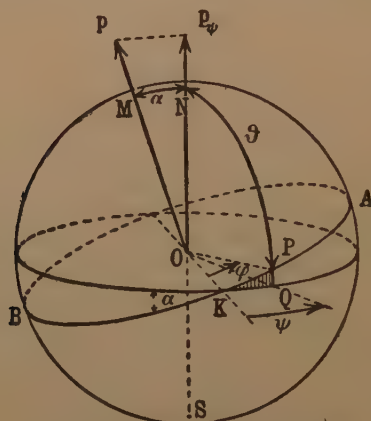


FIG. 12.—Quantization in Space.

quantization is carried out for the system when the field tends to a limiting value of zero. Now let α denote the angle between the plane of the orbit and the equatorial plane, i.e. α is the angle at K in the spherical triangle KQP. Then we have $\frac{p_\psi}{p_\phi} = \cos \alpha$. Substituting the values we have already found for

p_ψ and p_ϕ , we see that $\cos \alpha = \frac{m}{k}$. Reasons are given by Sommerfeld for excluding the value $m = 0$, which would mean that the plane of the orbit can be parallel to the applied field. Excluding this case we are left with k possible orientations in an external field, the possible orientations being given by

$$\cos \alpha = \frac{1}{k}, \frac{2}{k}, \frac{3}{k}, \dots, \frac{k}{k}.$$

As the electron can move round the orbit in opposite directions there will be twice as many states as there are orbits.

To illustrate this result, let us consider in particular the simple cases $k = 1$, $k = 2$, $k = 3$. These are shown in Fig. 13 :

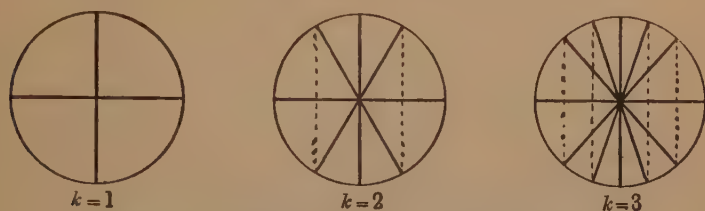


FIG. 13.—Spatial Position of Orbital Planes.

When $k = 1$, as the value $\alpha = \frac{\pi}{2}$ is excluded, we are left with only one possibility, namely when $\cos \alpha$ is unity, and therefore α is zero. The orbital plane coincides with the equatorial plane. But there are two possible senses for the rotation of the electron, in this plane, and so we get two possible states for our atom.

When $k = 2$ there are two possible values of α given by $\cos \alpha = \frac{1}{2}$ and $\cos \alpha = \frac{2}{2} = 1$. Consequently α is either 60° or zero. This means that besides the equatorial plane there is another possible inclination of the orbital plane, namely at an angle of 60° with the equatorial plane. The orbital plane, inclined at 60° , can be rotated arbitrarily about the direction of the lines of force.

When $k = 3$ there are three possibilities, $\cos \alpha = \frac{1}{3}$, $\cos \alpha = \frac{2}{3}$, $\cos \alpha = \frac{3}{3} = 1$. In each of these orientations in space the electron may describe either circular or elliptic orbits. It should be mentioned that in this simple treatment both the core and the electron have been regarded as possessing no magnetic properties. Sommerfeld remarks: "Without doubt this spatial quantizing is one of the most surprising results of the quantum theory. When we consider the simplicity with which the positions are derived and how simple is the result, it seems almost like magic."

We see, then, that for what may be termed the "one-quantum" atom there are two positions, and two only, for the vector of the magnetic moment in the magnetic field. These correspond to the two directions of rotation in the figure, and may be called the parallel and the anti-parallel positions. It may be supposed that one half of the atoms assume the first position, and the other half the second. That may seem surprising if we think of material magnets, because we are not

accustomed to a material magnet setting with its axis in opposition to the field, but with these elementary magnets the case is different. Let us consider, then, an atom possessing a magnetic moment $\pm M$, with the vector in the direction of the field, i.e. either in the parallel or in the anti-parallel position. When the field is not homogeneous such an atom will experience a mechanical force proportional to the magnetic moment and to the gradient of the field, i.e. to $\frac{\partial H}{\partial s}$ where H is the field strength, and s is distance measured in the direction of the field gradient. We know that a simple magnet placed in a uniform field merely turns on its axis but does not move bodily. When the field is not uniform, forces tending to produce translation do arise, and are determined by the product of M and the gradient of the field.

Let a stream of these magnetic atoms impinge and make a record on a plate perpendicular to their direction of motion. Then if the stream has a circular cross section, in the absence of a field the trace will be a small circle. When the field is applied, two circles should be seen if it be supposed that all the atoms have the same velocity, for the magnetic moment in the direction of the field may be either positive or negative. If, however, the velocities are distributed according to Maxwell's law, the traces will be elongated, but there should be a *minimum* effect in the undisplaced position.

On the classical theory all orientations are equally probable, and it can be shown that with Maxwellian distribution of velocities there should be an intensity *maximum* in the zero position.

Here then, there is a marked difference between the results given by the two theories, and this affords a crucial method for distinguishing between them.

2. The Experiments of Gerlach and Stern

Striking confirmation of the theory of quantization in space ("direction quantization") has been afforded by the wonderful experiments of Gerlach and Stern.* A stream of atoms of vaporized silver was allowed to flow in a high vacuum of the order 10^{-4} to 10^{-5} mm. of mercury, past the edge of the wedge-shaped pole of an electromagnet which produced a strong but non-uniform magnetic field. The silver atoms were deposited as a thin invisible layer on a glass plate placed immediately

* Gerlach and Stern, *Zeits. f. Physik*, vol. 8, p. 110, 1921; vol. 9, pp. 349 and 353, 1922.

behind the magnetic pole. When this layer was developed photographically it was found that there were two distinct, sharply-defined bands, indicating that the silver atoms were sorted out into two distinct and separate beams. The positions of the images on the plate showed that the atoms in one beam had been attracted towards the pole, and those in the other beam had been repelled, the attraction being slightly greater than the repulsion. When the electromagnet was not excited, no undeflected beam could be detected.

These results, then, give remarkable support to the quantum theory and to the principle of quantization in space. It was concluded from these experiments that all the silver atoms in the stream possessed a definite moment. From their measurements of the separation between the two limbs of the loop formed on the plate, Gerlach and Stern deduced the magnetic moment of the normal silver atom in the gaseous state, and found it to be, within the limits of experimental error, one Bohr magneton. This magneton is the value deduced on Bohr's theory for an electron describing a r_1 circular orbit. In the earlier experiments the error was of the order of 10 per cent. ; but later investigation reduced the error to something like 2 per cent.

In these experiments, the atoms, after passing through various openings, enter a chamber evacuated so that the free path of the molecules in it is very large compared with the dimensions of the space. The atoms pass through the opening into the chamber at such intervals that, in spite of the fact that their velocities are distributed according to Maxwell's law, there are few or no collisions. For these atoms in the stream, which may be made quite narrow, Gerlach * suggests the name "atomic rays" (Atomstrahlen).

It would appear, then, that while atoms of silver are passing through the magnetic field their magnetic axes have two distinct orientations in space. The difficult question as to how the magnetic atoms can alter their direction at all under the influence of a magnetic field has been discussed by Einstein and Ehrenfest.† Experiments in continuation of the original work of Gerlach and Stern have been carried out by other investigators, notably by Gerlach and Cilliers,‡ and by Gerlach§ himself. The results of these investigations are of such great importance that some further account of the method appears desirable. In Fig. 14 (p. 88) we have a diagrammatic representation of the apparatus.

* Gerlach, *Ann. d. Physik*, vol. 76, p. 106, 1925.

† Einstein and Ehrenfest, *Zeits. f. Physik*, vol. 11, p. 31, 1922.

‡ Gerlach and Cilliers, *Zeits. f. Physik*, vol. 26, p. 106, 1924.

§ Gerlach, *Ann. d. Physik*, vol. 76, p. 163, 1925.

The element to be examined was heated in a small electric oven, surrounded by a cooling chamber, and the metallic vapour escaping through an aperture in one wall of the oven passed through a system of slits S_1 and S_2 so as to produce a narrow stream of atoms, all travelling in the same direction. This stream passes through a non-homogeneous magnetic field produced by the pole pieces of an electromagnet, the pole pieces having the form shown at b on the right of Fig. 14. One pole piece is in the shape of a blunt wedge, the angle of the wedge being 90° in some cases and 60° in others. The opposing pole piece is provided with a groove parallel to the edge of the wedge. It was found that this arrangement gave a suitable non-uniform magnetic field. The stream of atoms having passed through the magnetic field, which in one form of the apparatus had a length of 3 cms. and in another about $4\frac{1}{2}$ cms., fell on a glass plate. The apparatus was enclosed in a gas-tight vessel which could be evacuated. The main difficulty in the earlier experi-

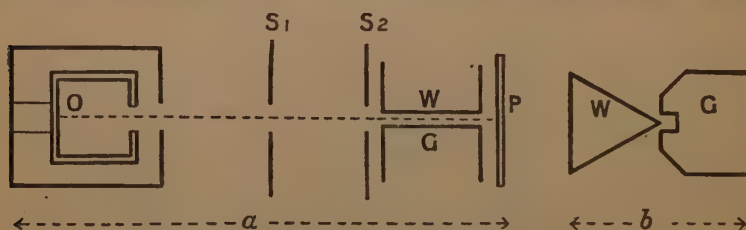


FIG. 14.—Experiments of Gerlach and Stern.

ments was the adjustment of the various parts in a straight line so as to give a rectilinear stream. This was overcome by reconstructing the apparatus so that the essential parts were fixed firmly to the magnet poles. In these later experiments the amount of silver deposited was so much increased that the displaced images could be seen without development, but no trace of a null line, which would be expected on the classical theory, could be obtained even after development.

It was found that under normal conditions copper and gold atoms behaved like silver atoms and showed the separation into two streams. The measurements indicate monatomic structure and a magnetic moment equal to that of the Bohr magneton. The atom of thallium has a smaller magnetic moment and appears to correspond to the case of $\pm \frac{1}{3}$ of a Bohr magneton. Lead, tin and iron atoms are not affected by the magnetic field, so apparently the atoms are non-magnetic. In the case of nickel the values indicated for the magnetic moment are ± 2 Bohr magnetons and also zero.

3. Later Experiments

Recently experiments have been carried out in America by J. B. Taylor.* He has modified the apparatus of Gerlach and Stern so as to be able to determine the magnetic moments of sodium and potassium atoms. He first repeated the experiment of Stern and Gerlach for silver atoms, using a silver-plated tungsten coil heated electrically as a source of the atoms instead of the furnace employed by the first experimenters. This simplified the procedure as there is considerable difficulty in ridding the furnace of gas. The slits employed were too wide to show more than a decided broadening of the image with a trace of division in some of the plates. In the experiments on sodium and potassium the slits were made narrower (0.03 mm.).

"The metals were evaporated into the apparatus at 345° C. and 245° C. respectively, and the images formed by the deposition of the atomic rays on cool glass strips were rendered visible by immersing the strips in hydrochloric acid gas, whereupon films of opaque chloride were formed. Both metals were found to possess an atomic moment of one Bohr magneton, within the limits of experimental error, which were about ten per cent."

The question as to whether molecules as a whole assume quantum orientations in a magnetic field has been brought into prominence by the experiments of Glaser.† Although the so-called Glaser anomaly has not been confirmed by later experimenters, some reference to the question seems called for. He investigated the magnetic susceptibility of the gases hydrogen, nitrogen and carbon dioxide at low pressures by means of a very sensitive form of Curie balance. On the classical theory the susceptibility should be proportional to the pressure of the gas. This was not in agreement with the experiments. Glaser suggested that his results, which cannot be explained by the classical theory, depend on the relative values of the times taken by the molecules to turn in the direction of the field and the times between molecular collisions, the ratio between these two times depending on the pressures and fields employed. On the other hand Lehrer‡ has found proportionality between volume susceptibility and pressure both for carbon dioxide and for argon; Hammar§ finds no evidence of a magnetic anomaly, though with imperfectly dried gases he obtains curves not unlike those of Glaser.

* Taylor, *Phys. Rev.*, vol. 28, p. 576, 1926.

† Glaser, *Ann. d. Physik*, vol. 75, p. 459, 1924.

‡ Lehrer, *Zeits. f. Physik*, vol. 37, p. 155, 1926; *Ann. d. Physik*, vol. 81, p. 229, 1926.

§ Hammar, *Proc. Nat. Acad. Sci.*, vol. 12, p. 594, 1926.

The experimental basis for the supposition of molecular orientation in polyatomic gases is thus rendered very uncertain ; in any case Glaser's explanation is not altogether satisfactory, for as Pauli* has pointed out, the total quantum numbers for the majority of the molecules, and therefore the numbers of possible orientations, are so large that the molecules might almost be regarded as orientated in all directions. The same argument tells against any alteration of refractive index of such a gas on applying a magnetic field transversely to the direction of propagation of the light. Ghosh and Mahanti† have reported such an alteration in the refractive index of carbon dioxide, but this is not confirmed by Appleyard.‡ Krishnan§ has searched for a double refraction under the same conditions as those in the experiments of Ghosh and Mahanti, but the results were uniformly negative.

REFERENCE

C. G. Darwin (*Proc. Roy. Soc.*, vol. 117, p. 258, 1927) has treated the theory of the Stern-Gerlach experiment from the standpoint of the new undulatory mechanics, and has shown that a satisfactory explanation of the results is obtained by treating the electron as a wave.

* Pauli, *Phys. Zeits.*, vol. 26, p. 217, 1925.

† Ghosh and Mahanti, *Nature*, vol. 118, p. 734, 1926.

‡ Appleyard, *Nature*, vol. 119, p. 353, 1927.

§ Krishnan, *Proc. Ind. Assoc. Cult. Sci.*, vol. 10, p. 35, 1926.

CHAPTER VII

MAGNETISM

In emphasizing the fact that there are many unsolved problems, the remarkable achievement of the quantum theory should not be forgotten. In the course of but a few years, the new outlook has enabled an extensive series of apparently disconnected phenomena to be correlated and interpreted, and as a result of the clear conception which has been obtained of the essential significance of atomic magnetism, the special study of the magnetic properties of atoms will be able to contribute more and more towards the solution of the problems of atomic structure generally.

E. C. STONER, *Magnetism and Atomic Structure*, 1926

1. Diamagnetism

DIAMAGNETISM is a property common to all matter, and on the classical theory is regarded as due to a Larmor precession of electronic orbits, similar to that which is accountable for the Zeeman effect. On this may be superimposed a larger paramagnetic effect due to change in the orientation of unbalanced electronic orbits. A considerable amount of experimental work has been carried out by Pascal, who has investigated the influence of chemical combination on the magnetic properties. It is found that diamagnetic atoms combine to give diamagnetic molecules, and the effects are approximately additive.

Langevin has given a theoretical discussion of diamagnetism and shown how an expression for the diamagnetic susceptibility may be obtained.

The diamagnetic susceptibility may be calculated by finding the changes in the nature of the orbits produced by the magnetic field. For simplicity we suppose that the electron orbits are circular and that their planes are perpendicular to the inducing field. When ν , the number of revolutions per second, is very great, the circling electron may be regarded as equivalent to an electric current of strength νe . The magnetic moment of the equivalent magnet will be νeA , where A is the area of the orbit. For a circular orbit of radius r the magnetic moment

$$\begin{aligned} M &= \nu e \pi r^2 \\ &= \frac{1}{2} e r^2 \omega, \quad \dots \dots \dots 7:1 \end{aligned}$$

where ω is the angular velocity of the electron.

We assume that the intensity of the magnetic field increases from zero to some final value H_e , and that the time required to reach this value is long in comparison with the periodic time of the electron in its orbit. We seek to find the change in the magnetic moment due to this applied field, and we shall assume as the result of a more exact investigation that the variation in the radius of the orbit is so small as to be negligible. In consequence of the variation in the strength of the magnetic field there will be an electromotive force E in the orbit, equal to the rate of decrease of the magnetic flux, i.e.

$$E = -\frac{d}{dt}(H\pi r^2) \quad . \quad . \quad . \quad 7:2$$

In one revolution the electron must do an amount of work eE . As the electron is revolving so rapidly the value of dH/dt changes very slightly in this revolution. We may then regard the work done by the electron as done against a constant force $F = eE/2\pi r$.

The equation of motion of the electron along the tangent to the orbit is therefore

$$\frac{m}{r} \frac{d}{dt}(r^2\omega) = \frac{eE}{2\pi r},$$

or

$$\frac{m}{r} \frac{d}{dt}\left(\frac{2M}{e}\right) = -\frac{e}{2\pi r} \frac{d}{dt}(H\pi r^2) \quad . \quad . \quad 7:3$$

Hence

$$\frac{dM}{dt} = -\frac{e^2}{4m} \frac{d}{dt}(Hr^2) \quad . \quad . \quad 7:4$$

Integrating this equation from the time $t=0$, when $H=0$ to the time when the magnetic field is established, we find for the whole change in the magnetic moment

$$\delta M = -\frac{e^2}{4m} H_e r_e^2 \quad . \quad . \quad . \quad 7:5$$

We notice that this change in the magnetic moment is independent of ω , and has the same sign for all the orbits even though the electrons may be revolving in opposite directions. If there are N orbits in unit volume and r is the mean square radius of an orbit, the intensity of magnetization acquired is

$I = -\frac{Ne^2 r^2}{4m} H_e$, and consequently the susceptibility is given by

$$\kappa = \frac{I}{H_e} = -\frac{Ne^2 r^2}{4m} \quad . \quad . \quad . \quad 7:6$$

Since κ is negative, the substance will appear diamagnetic.

We may draw attention to the fact that the change in the

magnetic moment may be regarded as brought about by an increase $\delta\omega \equiv 0$ in the angular velocity given by

$$0 = -\frac{eH_e}{2m} \quad . \quad . \quad . \quad . \quad . \quad 7:7$$

in accordance with the general result stated by Larmor.

Langevin's theory enables us to calculate the mean square radius of all the electronic orbits in the atom from the atomic diamagnetic susceptibility. The actual magnitudes of the diamagnetic constants give values for the mean square radius of the same order as those deduced from other evidence for hydrogen, carbon and nitrogen. For the inert gases the susceptibilities as at first determined were far too large to be compatible with the sizes of the atoms suggested by the Bohr theory, but a direct determination by Wills and Hector* has removed this discrepancy. The values agree with those predicted by Joos from the electron arrangements.

2. Paramagnetism and Ferromagnetism

In paramagnetic substances the susceptibility is small, though usually larger numerically than for diamagnetic substances, but it is positive instead of negative. In 1895 Curie found that the specific susceptibility χ (i.e. the susceptibility per unit mass) is inversely proportional to the absolute temperature and is independent of the strength of the field. Thus $\chi T = C$ where C is Curie's constant.

Ferromagnetic substances, including iron, nickel, cobalt and some alloys, have large positive values for the susceptibility, and these values depend on the past history of the material. These substances can be permanently magnetized and show the phenomenon of hysteresis. The specific susceptibility varies with temperature in a complicated manner. At a certain temperature called the "Curie Point" ferromagnetic substances lose most of their magnetic moment and become paramagnetic.

The electronic theory of paramagnetism advanced by Langevin is strictly applicable only to a paramagnetic gas, such as oxygen. On this theory the aggregate magnetic moment of the electronic orbits in the molecule is not zero, and it is assumed that the molecular magnet tends to turn in a magnetic field in such a direction that the potential energy in the field is a minimum. It is not easy to understand the mechanism of this orientation, as it cannot be produced *directly* by the field. It is customary

* Wills and Hector, *Phys. Rev.*, vol. 23, p. 209, 1924; Hector, *Phys. Rev.*, vol. 24, p. 418, 1924.

to assume that the changes in orientation are brought about by the processes by which temperature equilibrium is maintained, that is primarily by collisions between the molecules.

Langevin* assumed the molecules of the gas to be small magnets of equal magnetic moment M . Before the application of the magnetic field H the axes of the magnets are assumed to have a random distribution, but this uniform distribution of the axes is slightly disturbed by the action of the field. In the final state of the system a condition of statistical equilibrium is reached in which two tendencies balance one another; these are the tendency to set in a particular direction under the action of the field and the tendency to set equally in all directions as the result of thermal agitation and collisions. Langevin assumes that the law of distribution in the final state is the same as that which governs the density of a gas acted on by the force of gravity. The result of the mathematical investigation is to give for the resultant magnetic moment I of the N molecules considered

$$I = NM \left(\coth a - \frac{1}{a} \right) \quad . \quad . \quad . \quad . \quad 7:8$$

where $a = \frac{MH}{kT}$, k being Boltzmann's constant and T the absolute temperature.

Since NM is the saturation value of the magnetic moment, we denote it by I_0 , and then we have

$$I = I_0 \left(\coth a - \frac{1}{a} \right) \quad . \quad . \quad . \quad . \quad 7:9$$

At ordinary temperatures, even with the highest field available a will be very small, and it will be sufficiently accurate to retain the first term in the expression for I , giving

$$I = \frac{I_0 a}{3} = \frac{I_0 MH}{3kT} \quad . \quad . \quad . \quad . \quad 7:10$$

Consequently the magnetic susceptibility I/H is given by

$$\frac{MI_0}{3kT} = \frac{NM^2}{3kT} \quad . \quad . \quad . \quad . \quad 7:11$$

In applying this formula we must be careful to take N as the number of molecules per unit volume, or per unit mass, according as we wish to find the volume susceptibility or the specific susceptibility. When we are dealing with the gram molecule (1 mole) of gas we find

$$\chi = \frac{NM^2}{3kT} = \frac{N^2 M^2}{3RT} \quad . \quad . \quad . \quad . \quad 7:12$$

where R is the gas constant per mole.

* Langevin, *Ann. de Chim. et Phys.*, vol. 5, p. 70, 1905.

Honda and Okubo * have developed a theory of magnetism taking into account the rotational motion of the molecules, and have obtained an expression somewhat similar to that of Langevin.

In dealing with a paramagnetic solid it is necessary to take into account the mutual action between the solid molecules in forming an estimate of the resultant orientation. The effect of taking this action into account may be regarded as equivalent to increasing the kinetic energy by a certain amount. If we assume further that this amount is a constant independent of temperature, the resulting value for the susceptibility takes the form

$$\chi = \frac{N^2 M^2}{3R(T + \Delta)} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad 7:13$$

where Δ is a constant.

This relation was given by Onnes and Perrier, and was found to hold for a number of solid substances at low temperatures.

Langevin's theory of a paramagnetic gas has been extended by Weiss † so as to include paramagnetic substances generally, and also ferromagnetic substances. For this purpose he postulates the existence of a "molecular field" proportional to the intensity of magnetization acquired. Weiss assumed that the Weber elements, whatever they may be, in a ferromagnetic solid are free to rotate, but that they are subject, as regards rotation, only to constraints arising from the molecular field. His hypothesis enables us to co-ordinate a very large number of facts, but the nature of the molecular field remains a mystery. Weiss himself came to the conclusion that it is improbable that it can have a magnetic origin. Thus it appears that the classical theory of magnetism is left with two unsolved problems, the nature of the molecular field and the nature of the Weber elements.

3. The Quantum Theory of Paramagnetism

Many attempts have been made to apply the principle of the quantum theory in the subject of paramagnetism. Oosterhuis ‡ and Keesom, § in discussing the quantum theory of magnetism, proposed to substitute in formula 7:11 for the classical product kT corresponding to the mean energy of a degree of freedom, the quantum expression for the mean rotational

* Honda and Okubo, *Sci. Rep.*, vol. 7, p. 141, 1914.

† Weiss, *Journ. de Phys.*, vol. 6, p. 661, 1907; *Ann. de Phys.*, p. 134, 1914. An interesting review of this work on magnetism is to be found in *Le Magnétisme* by Weiss and Foex (Armand Colin, 1926).

‡ Oosterhuis, *Phys. Zeits.*, vol. 14, p. 862, 1913.

§ Keesom, *Phys. Zeits.*, vol. 15, p. 8, 1914.

energy. The application of the quantum theory was also considered by Gans* and by Weyssenhoff.† The latter made use of Planck's *second* quantum hypothesis, and assumed a single degree of freedom for the magnetic element, which was treated as a magnetic dipole with a fixed axis of rotation.

Reiche‡ developed a theory of paramagnetism in which the problem was regarded as one of two degrees of freedom, the axis of rotation being free and not fixed. By employing the differential equations of Jacobi and Hamilton he deduced a somewhat complicated expression for the molecular susceptibility, which may be written in the form:

$$\chi = \frac{5\pi^2 M^2 K N}{4h^2} \cdot \frac{e^{-\sigma} + \frac{4}{15} S_0}{S} \quad . \quad . \quad . \quad 7:12$$

Where $S_0 = \sum_2^{\infty} \frac{e^{-\sigma n^2}}{h(n^2 - 1)}$, $S = \sum_1^{\infty} n e^{-\sigma n^2}$, and $\sigma = \frac{h^2}{8\pi^2 K k T}$,

K being the moment of inertia of the magnetic element. Tables for the numerical evaluation of χ are given in his paper, but care must be taken, as pointed out by S. J. Barratt,§ to distinguish between the *molecular* and the *specific* susceptibility. When this point is attended to, the values for the susceptibility at high temperatures given by the quantum theory are in agreement with those found from the classical theory of Langevin and Weiss. The quantum theory gives a satisfactory representation of the variation of susceptibility with temperature.

We have seen in Chapter III that in studying the molecular susceptibility of magnetite, Weiss concluded that the magnetic moment of the molecule was always a multiple of a unit which may be called the magneton. Later Weiss noticed that the magnetic moments at saturation of iron and nickel at low temperatures were very nearly in the ratio of whole numbers, viz. 11:3, and came to the conclusion that atomic magnetic moments are multiples of the same fundamental unit. The value he found for this unit in 1911, reckoned per gram atom, was:

$$M_w = 1123.5 \text{ C.G.S. units.}$$

Thus at 20° on the absolute scale iron contains 11 magnetons, and nickel contains 3 magnetons. From measurements on solutions Weiss later on deduced a slightly larger value for the magneton, 1126 C.G.S. units, which he considered more accurate. Nevertheless magneton numbers are generally expressed in terms of the older unit. It must be clearly understood that the

* Gans, *Ann. d. Physik*, vol. 50, p. 163, 1916.

† Weyssenhoff, *Ann. d. Physik*, vol. 51, p. 285, 1916.

‡ Reiche, *Ann. d. Physik*, vol. 54, p. 401, 1917-8.

§ S. J. Barratt, *Ann. d. Physik*, vol. 77, p. 98, 1925.

magneton of Weiss is an empirical, and not a mechanistic deduction, and the experimental evidence in favour of such a unit is not sufficient to demonstrate its existence with any certainty. The Weiss magneton is convenient for the expression of atomic moments, but it is more than doubtful whether it is a true physical unit.

The Bohr magneton is, as we have seen, about five times as large as the Weiss magneton. There appears, then, to be a contradiction between the results of the quantum theory and the empirical results obtained by Weiss. Considerable light has been thrown on this problem by the work initiated by Pauli * who, for the first time, applied the principle of spatial quantizing to the individual magnetic molecules. According to Langevin's theory, for a paramagnetic gas the product of the specific magnetic susceptibility and the absolute temperature is a constant, determined by the product of M^2/R and the average value of $\cos^2\theta$.

$$\chi T = \frac{M^2}{R} \overline{\cos^2\theta}.$$

Here we have M as the magnetic moment of the gram atom, R is the gas constant for the same mass of gas, and θ is the angle between the magnetic axis of a gas molecule and the direction of the magnetic field. Langevin assumed θ to be continuously variable. The average value of $\cos^2\theta$ when all positions are regarded as equally probable, is found to be $\frac{1}{3}$. When, however, we adopt the point of view of quantization in space, only certain particular positions of the electron orbits which constitute the magnetons are possible. These favoured positions are determined, as we have seen previously, by taking $\cos\theta = \frac{1}{k}, \frac{2}{k}, \frac{3}{k} \dots \frac{k}{k}$.

When k is equal to unity, all the orbits are perpendicular to the lines of force, and in this case the average value of $\cos^2\theta$ is obviously 1. When $k = 2$, we must have either $\cos\theta = \frac{1}{2}$, or $\cos\theta = 1$, part of the orbits being perpendicular to the lines of force, part of them being at an angle of 30° to the lines of force. Consequently,

$$\overline{\cos^2\theta} = \frac{1}{2} \left[1 + \left(\frac{1}{2} \right)^2 \right] = \frac{5}{8}$$

In the general case, in which there are k equally probable positions, we find,

$$\overline{\cos^2\theta} = \frac{1}{k} \left[1 + \left(\frac{1}{k} \right)^2 + \left(\frac{2}{k} \right)^2 + \dots \right] = \frac{1}{3} \frac{(k+1)(2k+1)}{2k^2}.$$

In the limit, when k tends towards infinity, this reduces to Langevin's formula.

* W. Pauli, *Phys. Zeits.*, vol. 21, p. 615, 1920.

Corresponding to each value of h there will be a certain Bohr magneton value, and for each of these we can calculate the apparent Weiss magneton number, using the ordinary Langevin formula. Thus, in the case $h = 1$, Weiss would obtain a value too great by the factor $\sqrt{3}$. Instead, then, of five, as we might have expected, we shall have $p = 5\sqrt{3}$, or 8.7 instead of 5 Weiss magnetons. In the case $h = 2$, the method of calculation employed by Weiss would give $p = \frac{10\sqrt{3}}{\sqrt{\frac{8}{5}}}$ or 13.7, instead of

10 Weiss magnetons. As an example let us consider the two important paramagnetic gases, nitric oxide, NO, and oxygen, O₂. The values obtained are: 9.20 for NO, and 14.16 for O₂. These values suggest that in the case of NO we have to deal with *one* Bohr magneton, while for O₂ the result suggests that we have to do with *two* Bohr magnetons.* Pauli then suggests that when the results are calculated in this way we may, in certain cases, at least, obtain an integral number of Bohr magnetons. This is borne out by other results obtained both for crystals and for salt solutions. This point has been dealt with by Gerlach † and also by Epstein, ‡ and we are probably safe in concluding that the true unit is the Bohr magneton and not the Weiss magneton. Sommerfeld § has pointed out that the spectroscopic results dealing with "multiplets" lead to magneton numbers which support this conclusion, so that it appears certain that not only atoms or molecules in gases, but also ions in solutions, tend to take up definite orientations in a magnetic field which are determined by quantum conditions. Sommerfeld claims that the riddle of the magneton is now solved, the Weiss unit being only apparent, the unit of the quantum theory being real.

In later years considerable progress has been made in the quantum theory of paramagnetism. || Epstein and Gerlach have shown that the susceptibility of paramagnetic salts is independent of their being in solution or in the solid state, and that ions, whether in solution or in a space lattice, are arranged relatively to an external magnetic field in accordance with the quantum theory. The theory put forward by W. Pauli in 1920

* By applying the new quantum mechanics, together with recent spectroscopic data for nitric oxide, J. H. Van Vleck claims to have solved the difficulties of accounting numerically for the susceptibilities of these two gases (*Nature*, vol. 119, p. 670, 1927).

† Gerlach, *Phys. Zeits.*, vol. 24, p. 275, 1923.

‡ Epstein, *Science*, vol. 57, p. 532, 1923.

§ Sommerfeld, *Phys. Zeits.*, vol. 24, p. 360, 1923.

|| See a useful summary by Tamm, *Zeits. f. Physik*, vol. 32, p. 582, 1925.

"Our ordinary electrodynamic conceptions are probably insufficient to form a basis for an explanation of atomic magnetism. This is hardly to be wondered at when we remember that they have not proved adequate to account for the phenomena of radiation which are connected with the intimate interaction between the electric and magnetic forces arising from the motion of the electrons. In whatever way these difficulties may be solved it seems simplest to assume that the occurrence of magnetism, such as we meet in the elements of the fourth period, results from a lack of symmetry in the internal structure of the atom, thus preventing the magnetic forces arising from the motion of the electrons from forming a system of closed lines of force running wholly within the atom. While it has been assumed that the ions of the elements in the previous periods, whether positively or negatively charged, contain configurations of marked symmetrical character, we must, however, be prepared to encounter a definite lack of symmetry in the electronic configurations in ions of those elements within the fourth period which contain a group of electrons in 3-quanta orbits in the transition stage between symmetrical configurations of 8 and 18 electrons respectively. As pointed out by Kossel, the experimental results exhibit an extreme simplicity, the magnetic moment of the ions depending only on the number of electrons in the ion. Ferric ions, for example, exhibit the same atomic magnetism as manganous ions, while manganic ions exhibit the same atomic magnetism as chromous ions. It is in beautiful agreement with what we have assumed about the structure of the atoms of copper and zinc, that the magnetism disappears with these ions containing 28 electrons which, as I stated, must be assumed to contain a complete group of 3-quanta orbits. On the whole a consideration of the magnetic properties of the elements within the fourth period gives us a vivid impression of how a wound in the otherwise symmetrical inner structure is first developed and then healed as we pass from element to element. It is to be hoped that a further investigation of the magnetic properties will give us a clue to the way in which the group of electrons in 3-quanta orbits is developed step by step."

If we assume with Bohr that paramagnetism is independent of the nucleus of the atom but is governed entirely by the electronic orbits, we should expect the magnetic effect to be the same in all atoms with the same number of electrons even though the nuclear charges differ. This expectation is in accordance with the experimental results at present available. For example, the ferric ion, Fe^{+++} , and the manganous ion, Mn^{++} , both having 23 electrons, are similar in their magnetic properties.

A scheme for the distribution of electrons among atomic

levels differing somewhat from that of Bohr has been put forward independently by Main-Smith* and Stoner.†; This scheme, which has been discussed and developed by Sommerfeld,‡ particularly in its spectroscopic bearings, enables all the essential features involved in Bohr's picture of atom-building to be retained, but indicates a somewhat simpler mode of development. The suggested numbers of electrons in the sub-levels of the completed K, L, M . . . groups are : (2), (2,2,4), (2,2,4,4,6) . . . respectively. Support for such a distribution is derived from evidence based on considerations of intensities of X-ray lines, absorption of X-rays, optical spectra and chemical properties. It may be remarked in passing that the number of electrons in a sub-group is probably closely related to the "inner quantum number" (p. 62). As regards magnetic properties the ionic paramagnetism of the third-period elements is described by Stoner as follows : "The development of ions from K^+ or Ca^{++} (with 18 electrons) to Cu^+ (with 28 electrons) is brought about, in our view, by the simple addition of electrons to the M_{IV} and M_V sub-levels in 10 (4,6) orbits of the same nk type (3, 3).

Sommerfeld, taking into account spatial quantization, has shown§ that the number of Bohr magnetons associated with the ions increases regularly by steps of 1 from 0 to 5 (attaining this maximum value for Mn^{++} and Fe^{+++} with 23 electrons), and then decreases regularly to 0 (for Cu^+) with increasing numbers of electrons.

While the deeper meaning of this may be obscure, especially in that unit magnetic moment has apparently to be associated with (3,3) orbits, such a beautiful regularity is in agreement with the development of the M group by the simple addition of 10 similar (n, k) orbits; the presence of x electrons in the (M_{IV} and M_V) levels, superposed on completed groups, may be expected (by a sort of Babinet principle !) to produce the same paramagnetic properties as (10— x) electrons, for with the latter number the group diverges from non-paramagnetic completeness in the absence of x electrons. On the Bohr scheme, the development occurs by a complete re-organization of the whole M group from a (4,4) to a (6,6,6) arrangement. While the general nature of the change might be the same, the essential and striking feature—the regularity—would certainly not be anticipated.

The atomic magnetic properties of the elements have been fully discussed by Stoner in his valuable book on *Magnetism and Atomic Structure* (Methuen). He considers these properties

* Main-Smith, *Chemistry and Atomic Structure*, 1924.

† Stoner, *Phil. Mag.*, vol. 48, p. 719, 1924.

‡ Sommerfeld, *Phys. Zeits.*, vol. 26, p. 70, 1925.

§ Sommerfeld, *Zeits. f. Physik*, vol. 19, p. 221, 1923.

both in connection with successive elements forming a sequence and as regards the family relationships of analogous elements. We may emphasize his conclusion that the magnetic characteristics of the ions in the first transition series may be brought into relation with the spectra of these elements, though the correlation is at present by no means complete.* Hund † has treated the question of the ionic magnetic moments of the rare earths, and has shown how the magnetic constants may be computed from the quantum numbers of the electron orbits, employing Heisenberg's principles to find the probable ground terms of the ions.

"The survey of the periodic table shows that the magnetic properties of atoms, so far as they are known, fall into line with the chemical and spectroscopic properties, being generally capable of correlation in terms of the general quantum theory of atomic structure" (Stoner).

5. Magnetism and Chemical Combination

In the electronic theory of magnetism developed by Langevin ‡ the electrons are assumed to revolve in individual orbits, thus producing average effects similar to those of ordinary current circuits. Speaking of the electrons responsible for the magnetic properties of the molecule, he says (*loc. cit.*, p. 122) :

"These are perhaps the very same electrons, situated in the outer part of the system, forming the molecule, that play a part in chemical actions, where we know that electrons equal in number to the valence come into action."

It should be observed that Langevin does not specify that the chemical forces due to his electrons are magnetic in nature. Such an idea was at least suggested in the work of Weiss § on the magneton, for he asks: "What is the rôle of magnetic phenomena in chemical combination? Are chemical forces magnetic in nature? Are the valences, indeed, referable in some way to magnetons?" A. L. Parson || identified the electron with the magneton, and showed that many of the facts of chemistry receive an explanation by means of this assumption, special stress being laid on the stability of the group of eight magnetons. Parson was the first to point out the remarkable parallelism between chemical and magnetic unsaturation.

* Stoner has pointed out the difficulties that arise in dealing with these ions in a paper on "Magnetism and Molecular Structure," *Phil. Mag.*, vol. 3, p. 342, 1927.

† Hund, *Zeits. f. Physik*, vol. 33, p. 855, 1925.

‡ Langevin, *Ann. de Chim. et de Phys.*, vol. 5, pp. 70-127, 1905.

§ Weiss, *Journal de Physique*, [5] 1, pp. 900, 965, 1911.

|| Parson, *Smithsonian Misc. Coll.*, vol. 65, no. 11, 1915.

The pairing of electrons in the formation of chemical bonds, though a phenomenon of almost universal occurrence, was for a long time almost overlooked by physicists. But recent investigations from the physical side point to the phenomenon of pairing as being of importance in relation to ionization potentials and to spectroscopic observations. The chemical evidence for the coupling of two electrons has been considered in detail by G. N. Lewis * and by Langmuir,† and the former ‡ has discussed at length the "magneto-chemical theory" of valence. "When we state that the basic fact of chemistry is the pairing of electrons it would be more explicit to state that two isolated electronic orbits or magnets tend to couple with one another so as to eliminate their magnetic moments. The phenomenon is the same in principle, whether the two elementary magnets belong to a single atom or to separate atoms. In the latter case the pair which is formed is the joint property of two atoms and is known as the chemical bond." Perhaps the pair of electrons which is the most rigidly held is the one in the helium atom. In neon we have in addition a group of eight (octet) which may perhaps be regarded as a regular tetrahedron with a pair of electrons at each corner.

A. E. Oxley § has developed the view that electrons moving in small orbits may explain paramagnetic and diamagnetic linkages and also the behaviour of crystals in a magnetic field.

There exists a close relationship between the equilibrium positions of diamagnetic and paramagnetic crystalline bodies, suspended in a magnetic field, and the directions of the cleavage planes. This implies that the forces of cohesion in different directions are closely allied with the magnetic behaviour of the crystalline medium, and lead us to suspect that the forces of crystallization are in part, at least, of a magnetic nature. A complete theory is only possible if due consideration be given to both the magnetic and the electrostatic forces, the former preponderating in some cases, the latter in others. In any case it is clear that the magnetic forces cannot be ignored.

Reference may also be made to the suggestions for a magnetic theory of valency put forward by A. P. Laurie.||

* Lewis, *Journ. Amer. Chem. Soc.*, vol. 38, p. 762, 1916.

† Langmuir, *Journ. Amer. Chem. Soc.*, vol. 41, p. 868, 1919.

‡ G. N. Lewis, "Valence and the Structure of Atoms and Molecules," *Amer. Chem. Soc. Monographs*, 1923. "The Magnetochemical Theory," *Chemical Reviews*, Vol. I, No. 2, July, 1924.

§ Oxley, *Proc. Roy. Soc. A*, vol. 98, p. 264, 1920; vol. 101, p. 264, 1922. *Science Progress*, No. 56, March, 1920.

|| Laurie, *Proc. Roy. Soc. Edin.*, vol. 42, p. 352, 1921-2; vol. 43, p. 72, 1922-3; *Faraday Soc. Trans.*, vol. 20, p. 1, 1924.

The rôle of magnetism in valence has been discussed by E. H. Williams* who emphasizes the scarcity of "odd molecules," i.e. molecules having an odd number of electrons, amongst chemical compounds. Many physical phenomena seem to be largely dependent on whether the atom or molecule contains an odd or an even number of electrons; amongst these properties may be instanced the ionization potential† and the multiplicity of spectral lines. It may be assumed that when there is an even number of electrons in the atom they will group themselves in pairs in such a manner as to neutralize each other and thus produce diamagnetism, whereas when the number is odd there will necessarily be one electron that cannot be paired and this will produce external effects if not neutralized by an electron in some other atom. In this connection the possibility of magnetism being one of the factors in valence comes in. One of the tests in favour of a magnetochemical theory of valence would be the change of a paramagnetic substance to a diamagnetic substance when the valence is modified so as to change the molecule from one of odd molecular number to one of even molecular number. A number of instances of his kind are given, but on the other hand MnO (odd) and Mn_2O_3 (even) are both paramagnetic. Similar conclusions have been reached by Shaffer and Taylor.‡

Sommerfeld § considers that chemical combination is determined by the tendency to complete the outermost shell of electrons of an atom, and there is considerable evidence that the tendency to complete a sub-group n_{kj} , is effective in this respect, as well as the tendency to complete a group n_k .

We have already seen that atomic (or ionic) spectral, chemical and magnetic properties can be closely correlated. Stoner || has made a beginning at the correlation of these properties for the simpler molecules. The study of band spectra has led spectroscopists to the conclusion that the energy levels associated with the valence electrons of molecules are very similar to those associated with the valence electrons of atoms. If now the systems of energy levels of the molecule and of a "corresponding" atom are essentially similar, the electronic structure responsible for the two systems must also be essentially similar. As an illustration, Stoner endeavours to form a rough picture of

* E. H. Williams, *Phys. Rev.*, vol. 28, p. 167, 1926.

† F. A. Saunders, *Science*, vol. 59, p. 47, 1924.

‡ S. S. Shaffer and N. W. Taylor, *Journ. Am. Chem. Soc.*, vol. 48, pp. 483, 854, 1926.

§ Sommerfeld, *Manchester Lit. and Phil. Soc.*, vol. 70, 1926; *Nature*, vol. 117, p. 793, 1926.

|| Stoner, *Phil. Mag.*, vol. 3, p. 336, 1927.

molecular systems of the type CN, BO, and CO^+ , which have 13 electrons, of which 4 may be assumed to be K electrons. Each nucleus has a pair of K electrons moving in small firmly-bound orbits associated with it; the bi-nuclear system rotates, and the nuclei oscillate along the line joining them; the whole of this system acts as a single nucleus for the 9 outer electrons which distribute themselves among orbits in a similar way to electrons in atoms. Probably 8 of the outer electrons form a closed configuration similar to that of the 8 L electrons in neon, and the remaining electron moves in orbits similar to those of the valence electron in sodium. All such molecular models will, however, require revision in the light of the new theories of quantum mechanics and the hypothesis of the spinning electron.

6. Magnetism and Angular Momentum—Gyromagnetic Ratio

“Ampère’s assumption that the elementary magnet, or magneton, is a permanent whirl of electricity, and Weber’s assumption that electricity in general, and that of Ampère’s whirls in particular, has mass, require together that the elementary magnet should possess angular momentum, unless it is constituted of both positive and negative electricities rotating in opposite directions. In this case a finite magnetic moment *might* be accompanied with no angular momentum. If the magneton has angular momentum, it must exhibit the dynamical properties of a gyroscope. Furthermore, if all the magnetons in a magnetized body or magnet have angular momentum in the same direction or if the angular momentum in one direction is preponderant, the whole magnet must behave like a gyroscope. Similarly, a coil of wire traversed by an electric current consisting of a stream of one kind of electrons only, or with the linear momentum of one kind preponderant, must have angular momentum.”* Thus we might expect to find in magnetic material in bulk that magnetization may be accompanied by rotation and rotation by magnetization.

In 1861 Maxwell made attempts to detect the angular momentum of electricity flowing in a coil of wire or the angular momentum of Ampèreian whirls in magnetic matter, but concluded that if a magnet contains matter in rapid rotation, the angular momentum of this rotation must be very small compared with any quantities which we can measure.†

* S. J. Barnett, “The Angular Momentum of the Elementary Magnet,” *Bull. Nat. Research Council*, vol. 3, p. 235, 1922.

† Maxwell, *Electricity and Magnetism*, 574, 575.

Many years later several experimenters attempted to detect a change in the magnetization of an iron rod produced by rotating it about its axis, the first successful experiments of this kind being made by S. J. Barnett * in 1914. If the magneton be assumed to consist of a symmetrical electrical system rotating about the axis of symmetry, the electrical charge in rotation being all of one sign, a simple quantitative theory shows that rotating a body so that it makes N revolutions per second will produce the same intensity of magnetization in it as placing it in a magnetic field of strength, $2\pi RN$ gauss. Here R denotes the ratio of the angular momentum of the magneton to its magnetic moment, and is called the *gyromagnetic ratio*. This assumes that all the magnetons in the body are alike.

The theoretical value of the ratio R for three types of magnetons has been deduced with the following results.

(1) The magneton is assumed to consist of n similar electrons, each of mass m and charge e revolving in a circular orbit about a fixed nucleus, carrying a charge ne of the opposite sign.

Then
$$R = 2m/e.$$

If the distance between successive electrons in the orbit is comparable with the diameter of an electron, m will be greater than the mass of the free electron.

(2) The magneton of Voigt consists of a homogeneous uniformly charged solid in rotation. No account is taken of the electromagnetic origin of the mass, but the mass density is taken as everywhere proportional to the electric density. The result is the same as in the case of an electron ring.

$$R = 2m/e.$$

(3) Abraham has calculated the angular momentum of a spherical electron in rotation on the assumption that the mass and momentum are purely electromagnetic.

For a uniform surface charge, $R = m/e$.

For a uniform volume charge, $R = \frac{5}{4} m/e$.

The first of these is just one-half the value for an electron orbit, and the second somewhat smaller.

As the result of an elaborate series of experiments extending over a number of years Barnett finds for steel, soft iron, cobalt, nickel and Heusler alloy, the value $R = m/e$ within the limits of experimental error. "The value obtained for R shows either that negative magnetons, such as that of Abraham, with a value of R much less than that for an orbital ring are responsible for magnetism, or else that positive electrons or

* S. J. Barnett, *Phys. Rev.*, vol. 6, p. 239, 1915.

magnetons, whose rotation produces an opposite effect, are also involved."

In 1908, O. W. Richardson * suggested that when a bar of iron is magnetized, we might expect to observe a rotational mechanical reaction, and he calculated from an electronic standpoint the value of the gyromagnetic ratio. This effect was first detected and measured experimentally by Einstein and de Haas, † but after many improvements introduced by successive experimenters (notably by Stewart and by Chattock and Bates), the conclusion has been reached that the angular momentum arising in a ferro-magnetic substance from unit change in its magnetic moment is very nearly, if not exactly, one-half the value predicted by the simple formula $R = 2m/e$. The experimental value is in general agreement with that deduced by Barnett ‡ from experiments on the converse effect.

To account for the observed value of the gyromagnetic ratio Richardson concludes that the motions of the positively charged parts of the atoms cannot be disregarded. "It is necessary and sufficient, on this view of the phenomena, that in the establishment by magnetization of angular momentum the contribution arising from the positively charged parts of the atom should always be one-half of that from the negative electrons and oppositely directed to it." §

On the quantum theory it is possible to account for the facts by assuming that the magnetism of iron is due to a pair of parallel or co-planar orbits each having a single azimuthal quantum, and that another azimuthal quantum is assigned to the nucleus. "If this orbit turns with the field in the same sense as the two effective electron orbits, as the quantum conditions seem to require, its angular momentum will have to be oppositely directed to theirs."

A somewhat specialized form of the previous explanation of the gyromagnetic anomaly has been put forward later by Richardson. || The nucleus is supposed to have a quantized spin with angular momentum equal in magnitude to one half of, and opposite in sign to, that of all the electrons in the atom. For simplicity it is assumed that the nucleus may be treated as a uniformly charged non-conducting spherical surface kept from exploding by a uniform non-electromagnetic tension. Richardson deduces a value for the gyromagnetic ratio which agrees with

* Richardson, *Phys. Rev.*, vol. 26, p. 248, 1908.

† Einstein and de Haas, *Verh. Deutsch. Phys. Ges.*, vol. 17, p. 152, 1915.

‡ Barnett, *Phys. Rev.*, vol. 6, p. 239, 1915; vol. 10, p. 7, 1917.

§ O. W. Richardson, *Proc. Roy. Soc. A*, vol. 102, p. 538, 1923.

|| Richardson, *Proc. Phys. Soc.*, vol. 39, p. 173, 1927.

the value determined experimentally within the accuracy of the measurements.

A number of other proposals for explaining away the anomaly have been summarized and discussed by Stoner.*

* Stoner, *Magnetism and Atomic Structure*, p. 192.

PART II

SPECIAL INVESTIGATIONS

CHAPTER VIII

WHITTAKER'S QUANTUM MECHANISM IN THE ATOM

A science, like a planet, grows in the main by a process of infinitesimal accretion. Each research is usually a modification of a preceding one; each new theory is built like a cathedral through the addition by many builders of many different elements.

R. A. MILLIKAN, *The Electron* (1917)

1. Introductory : Special Investigations

IN Part I of this book we have considered the development of the quantum theory on what may be called orthodox lines. But in the history of science it is seldom found that the path of advance is straight forward. The goal is out of sight and many false starts may be made, many by-paths explored, before the band of explorers finds the best route for progress. And it does sometimes happen that the individual explorer following a lone trail reaches some result of importance which might have been missed by following the main line of advance. In the next few chapters we shall describe some investigations of a specialized character which are related only in an indirect manner to the Bohr theory. Those readers whose interest is confined to that theory may pass on to Part III, in which its further development is described. An account is also given there of the new quantum mechanics which may eventually supersede earlier theories.

2. The Interaction between an Atom and an Electron

In an important and very suggestive paper read before the Royal Society of Edinburgh on May 8, 1922, E. T. Whittaker *

* E. T. Whittaker, *Proc. Roy. Soc. Edin.*, vol. 42, p. 129, 1922.

described a mechanism within the atom so constituted as to compel all exchanges between the kinetic energy of electrons and radiant energy to take place in amounts $h\nu$, where h is Planck's constant and ν is the frequency of the radiation.

"It is now well established experimentally that when an atom is caused to emit radiation of frequency ν by collision with an electron, the amount U of kinetic energy of the electron which is absorbed by the atom is given by the equation

$$U = h\nu,$$

where h is Planck's quantum of Action: an electron whose kinetic energy before the encounter is less than $h\nu$ is incapable of stimulating the atom to emit the radiation, and is merely repelled from the atom without any loss of energy."

Whittaker considered the nature of the interaction between an atom and an approaching electron. Let us suppose that an electron is approaching an atom with a velocity which is not great enough to ionize the atom, but which may be great enough to evoke a "single-line spectrum" (Franck and Hertz, 1914).

"The experimental results indicate that the electron, as it approaches, experiences a repulsion which is sufficient to turn it back altogether if its kinetic energy is less than $h\nu$. We have first to determine the nature of this repulsion. Now there are two kinds of force which are capable of acting on the electron, namely, electric force and magnetic force, and we have to decide which of these two is operative in the present case. The decision is easy, since we know that motion through a field of electric force affects the kinetic energy of an atom, while motion through a field of magnetic force deflects its direction of motion without altering its energy: and in our case the fate of the electron depends entirely on whether it possesses enough kinetic energy to force its way through the field. The field must therefore be electric: that is to say, *an electron which is approaching an atom experiences, in the vicinity of the atom, a field of electric force.*"

"We have now to consider whether this field of electric force is always present in the vicinity of the atom, whether the electron is there or not, or whether the field is evoked in some way by the approach of the atom. Here again the decision is not in doubt: the atom cannot maintain a permanent electric field in this vicinity unless it either contains an excess of electricity of one sign, or is permanently polarized electrically; both of which suppositions are ruled out since the atoms considered are neutral atoms which do not respond to an ordinary electric field. We thus infer that *the electric field about an atom is not permanent, but is evoked by the approach of the electron.*

"We have now to consider what kind of mechanism within

the atom provides this responsive electric field when the electron approaches.

* * * * *

“What is wanted in our case is an electric analogue of the mechanism of induced magnetization in *diamagnetic* bodies. Induced magnetization in a diamagnetic body is, however, accounted for by supposing that the inducing magnet, as it approaches the body, induces electric currents in the atoms of the body. We are driven to conclude that a corresponding explanation, or at least a corresponding set of mathematical equations, applies in our case, and thus infer that *the electron, as it approaches the atom, induces within the atom a ‘magnetic current,’ that is, the magnetic analogue of an electric current: or at any rate, induces something which behaves like a magnetic current.*”

3. The Quantum Mechanism

Whittaker then proceeds to describe a structure which will provide the required “magnetic current.” This structure is essentially similar to one of those models which have been proposed by Sir Alfred Ewing for the purpose of explaining induced magnetization (p. 34). He imagines a number of bar magnets rigidly connected like the spokes of a wheel, having poles of the same name at the circumference, the corresponding poles of contrary name being at the centre. Such a structure may conveniently be termed a “magnetic wheel.”

Whittaker shows that when a bombarding electron, moving along the axis, approaches the wheel it sets the latter turning; the rotation of the wheel constituting a “magnetic current.” If the initial velocity of the bombarding electron falls short of a certain limiting value, the encounter is perfectly elastic: that is to say, the electron is reflected back without loss of energy. The point at which its direction of motion becomes reversed may be on either side of the plane of the wheel, depending on the electron's initial velocity of approach. If the initial velocity exceeds the stated limit, the electron passes clear through the system and escapes. But the electron escapes with a definite reduction of velocity corresponding to a quantum of energy which it has given up to the wheel. When the encounter is elastic, the angular velocity which the wheel acquires during the approach of the electron is lost during the return of the electron. When the encounter is not elastic, and the electron has passed clear through, the wheel is left rotating with a definite angular velocity, and the energy of rotation which the wheel now possesses represents the source of the consequent radiation.

Let us suppose that the radius of the circle in which the magnetic poles revolve is a , and let us take the axis of x as the axis of the wheel. When the magnetic wheel is rotating about the axis with angular velocity $\dot{\psi}$, it sets up by its motion an electric field. The electric field thus produced will exert a force on an electron (charge e , mass m) situated at a point on the axis at a distance x from the centre, equal to $Mea^2\dot{\psi}/(a^2 + x^2)^{3/2}$. Here M is the sum of the magnetic poles (of one sign) in the magnetic wheel. When the electron is moving along the axis, it creates a magnetic field which tends to set the wheel in rotation, the lines of magnetic force due to the electron moving in a straight line being circular, just as in the case of the linear electric current.

The equations of motion of the electron and of the magnetic wheel may be written in the form

$$m\ddot{x} + \frac{Mea^2\dot{\psi}}{(a^2 + x^2)^{3/2}} = 0 \quad . \quad . \quad . \quad 8:1$$

$$A\ddot{\psi} - \frac{Mea^2\dot{x}}{(a^2 + x^2)^{3/2}} = 0 \quad . \quad . \quad . \quad 8:2$$

In equation 8:2, which represents the motion of the wheel, A is the moment of inertia of the wheel. The two first integrals of these equations can be obtained without difficulty. One of these is the equation of conservation of energy, and is

$$\frac{1}{2}A\dot{\psi}^2 + \frac{1}{2}m\dot{x}^2 = \frac{1}{2}mu^2 \quad . \quad . \quad . \quad 8:3$$

assuming that initially, the wheel is at rest, and the electron is projected from $x = -\infty$ with velocity u . The second integral of the equations of motion is written by Whittaker in the form

$$A\dot{\psi} - \frac{Mex}{(a^2 + x^2)^{1/2}} = Me \quad . \quad . \quad . \quad 8:4$$

Equation 8:4 may be interpreted as representing conservation of angular momentum, provided we take into account angular momentum in the electromagnetic field. Adding Me to each side, the equation takes the form

$$A\dot{\psi} + Me \left\{ 1 - \frac{x}{(a^2 + x^2)^{1/2}} \right\} = 2Me \quad . \quad . \quad 8:5$$

or
$$A\dot{\psi} + \frac{Me\Omega}{2\pi} = 2Me \quad . \quad . \quad . \quad 8:6$$

where Ω denotes the solid angle subtended by the magnetic wheel at the electron. In equation 8:6 the first term represents the angular momentum of the magnetic wheel. The second term may be taken to represent the angular momentum in the field arising from the presence of the electron, and what is, essentially, a magneton. The result can be obtained from an

extension of McLaren's theorem (p. 41) with regard to the angular momentum of a magneton.

It follows from these equations that when the initial velocity u is small, the electron travels to a definite point on the axis where it comes to rest, and the motion is then reversed. When

$u = \frac{eM}{\sqrt{Am}}$, the electron is able to get just as far as the magnetic

structure, but not beyond it. When u is greater than this value, the point of reversal is on the further side of the magnetic struc-

ture. When, however, u has a value $\frac{2eM}{\sqrt{Am}}$, or any greater

value, the electron is able to pass completely through and out of the magnetic system, so as to be free from its influence.

In this latter case, the angular velocity ω (the final value of $\dot{\psi}$, corresponding to $x = \infty$) is given by the equation

$$A\omega = 2eM \quad . \quad . \quad . \quad . \quad . \quad 8:7$$

and an amount of energy $U = \frac{1}{2}A\omega^2 = \frac{2e^2M^2}{A}$ is lost by the

electron and gained by the magnetic structure. Unless the initial energy of the electron is as great as U , the electron gives up no energy to the magnetic structure, but experiences an "elastic impact." If, however, the initial energy of the electron is greater than U , it gives up exactly the amount U of energy, and retains the rest.

4. The Emission of Radiation

Now we turn to the transformation of the energy absorbed into the radiant form by the mechanism in the atom. The energy absorbed by the atom from the moving electron becomes resident in the atom as the energy of a magnetic current. Just as a closed electric current is equivalent to a magnetic shell, so a magnetic current is equivalent to an electric shell ; an electric shell being to all intents and purposes what is called a charged condenser, in electrostatics.

It is found that the charge on either plate of the condenser which is equivalent to the magnetic current is numerically equal to the charge on the bombarding electron. One might almost say that the passage of the electron through the structure has resulted in the formation of a positive and negative electron, an electric dipole. Now a Hertzian oscillator is essentially a condenser in the act of discharging, the frequency ν being given by the well-known equation

$$\nu = \frac{I}{2\pi\sqrt{LC}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 8 : 8$$

It is assumed that there are two factors associated with the vibrator in any particular atom which play the same part as the capacity C and the inductance L in the differential equation for the oscillatory discharge of a condenser.

Whittaker pointed out that $e^2\sqrt{L/C}$ has the same dimensions in every possible system of units, namely—the dimensions of mechanical action. This quantity, which may be regarded as a natural constant of action, is accordingly represented by h/π , and consequently,

$$\sqrt{\frac{L}{C}} = \frac{h}{\pi e^2} \quad . \quad . \quad . \quad . \quad . \quad 8:9$$

This may be taken to indicate that the Hertzian oscillators in the atoms are similar to each other in structure and differ only in scale.

From equations 8:8 and 8:9 we find

$$h\nu = \frac{e^2}{2C} \quad . \quad . \quad . \quad . \quad . \quad 8:10$$

The right-hand side of this equation represents the energy of the charged condenser, which, in turn, is equal to U , because the energy of the charged condenser is the energy of the magnetic wheel. Consequently we have

$$h\nu = U \quad . \quad . \quad . \quad . \quad . \quad 8:11$$

which is precisely Planck's equation connecting the frequency of the emitted radiation with the amount of kinetic energy absorbed from the bombarding electron.

It must be admitted that Whittaker's mechanism presents a very artificial appearance, and he himself recognizes clearly that we have here merely a model. It is the mathematical equations to which he attaches importance. He remarks that after having obtained a satisfactory system of equations, we may discard the model by which we have been led to it. He points out that instances of this in the history of Physics are abundant. "To name only the most famous of them, it was a model of rolling particles, idle wheels, and cellular vortices that suggested to Maxwell the correct differential equations of the æther. The model, having served its purpose, soon dropped out of sight: and the æther itself appears to be following it into oblivion. The differential equations alone remain, and in the hands of the relativists have provided the foundation for a complete reconstruction of our ideas of the universe."

5. Discussion of the Quantum Mechanism

The discussion of the mechanism falls naturally into two parts corresponding to the two processes: (1) the communication

of rotational energy to the magnetic wheel by the bombarding electron; (2) the conversion of this rotational energy into the oscillatory form required for radiation.

(1) Whittaker deals only with the case in which the bombarding electron moves along the axis of the magnetic wheel.

B. B. Baker * has investigated the more general case in which the motion of the electron is not restricted to the axis of the magnetic wheel, but may be in any direction initially. The results deduced are precisely the same as those obtained by Whittaker in the particular case which he considered: the electron can permanently transfer an amount of energy to the magnetic wheel only if its velocity and direction of projection are such that it penetrates the magnetic structure, and passes away out of the influence of the wheel without returning on its path. In such a case the wheel is finally left in rotation with an angular velocity $\omega = 2eM/A$, and the amount of kinetic energy U transferred from the electron to the structure is given by $U = 2e^2M^2/A$; in order to obtain this result the initial velocity of the electron must be at least as great as $2eM/\sqrt{Am}$.

The result has been generalized still further by H. A. Lorentz † who has taken into account the forces which may arise from the existence of a magnetic field. The magnetic wheel is treated as a circular ring over which magnetism is uniformly distributed. In an effective encounter the ring will receive an amount of energy U provided the rotation which may have been imparted to it by a previous encounter has first disappeared in one way or another.

Lorentz goes on to say: "What is especially interesting in Whittaker's idea seems to me to be this, that it shows the possibility of a sharp criterion, by means of which it can be decided whether an encounter is effective or otherwise. Such a criterion there must certainly be."

J. A. Eldridge ‡ has published a note on Whittaker's atomic model in which he draws attention to the difficulty arising from the presence of the poles at the centre of the wheel. When the forces on the central pole are taken into account it is found that the total angular impulse given to the wheel is zero.

Consequently, Eldridge concludes that the motion of the electron through the wheel does not set the wheel in permanent rotation. He goes on to say: "Whittaker has in effect employed a mechanism involving a unipolar magnet, and a unipolar magnet is a conception abhorrent to physics."

The objection here raised against Whittaker's quantum

* B. B. Baker, *Phil. Mag.*, vol. 44, p. 777, 1922.

† H. A. Lorentz, *K. Akad. Amst. Proc.*, vol. 25, p. 414, 1923.

‡ J. A. Eldridge, *Proc. Roy. Soc. Edin.*, vol. 45, p. 245, 1925.

mechanism in the atom, viz. that it implies the existence of unipolar magnets, is valid only in the particular case considered in which the electron moves along the axis of the magnetic wheel. In this case the electron has to pass through two rings of poles of contrary sign, and the angular impulse arising from the inner ring is exactly equal and opposite to the angular impulse from the outer ring.

There appears to be a possible way out of the difficulty if we suppose that the electron, instead of moving along the axis, is projected in such a manner that it passes through the ring composed of poles of one name, but not through the ring formed of poles of contrary name.

As illustrating the possibility of obtaining such rotations with ordinary bar magnets, we may recall the classical experiment of Faraday who produced the continued revolution of one of the poles of a magnet round a vertical conducting wire. In this experiment the whole magnet, with the exception of one extremity, was immersed in mercury, and the action of the wire carrying the current was limited almost entirely to the exposed pole. In modifications of the experiment,* frequently used for lecture demonstration, the magnet is suspended on a pivot and by means of mercury contacts the vertical current is made to pass near the upper pole only, the current being led off horizontally about the centre of the magnet. It was a model of this kind which suggested the possibility of meeting the difficulty raised by Eldridge in the manner described above.

In our previous work some physical significance has been attached to tubes of magnetic induction, and it is interesting to trace the distribution of the tubes in the case presented by Prof. Whittaker's magneton. Regarding the model as a wheel with a S-pole at the hub and N-poles distributed round the rim, the lines of force starting from the rim would curve round and enter the wheel at its centre. The number of tubes N , is 4π times the total pole strength, i.e. $N = 4\pi M$, where M denotes the sum of the poles (of one sign) of the different bar magnets which form the spokes of the wheel.

Now equation 8:7 gives $A\omega = 2eM$, i.e., the angular momentum $= 2eM = \frac{1}{2\pi}Ne$.

According to Nicholson's hypothesis angular momentum can be expressed as $nh/2\pi$. Equating these expressions, $\frac{1}{2\pi}Ne = nh/2\pi$, and thus we get $N = n(h/e)$. That is, the total number of magnetic tubes associated with the magneton is an

* Francis Watkins, *A Popular Sketch of Electro-magnetism and Electrodynamics*, 1828; P. M. Roget, *Treatise on Electro-magnetism*, 1832.

integral number of times the fundamental quantum tube defined by h/e , in exact agreement with previous results.

It may be noted that the angular momentum is independent of the size of the magnetic wheel.

The general arrangement of the lines of magnetic force in the model is not unlike that which would occur if two thin anchor rings, representing the magnetons either of McLaren or of Parson, were placed near together with their planes parallel and having a common axis. Thus, if we think of Whittaker's magneton as a bicycle wheel, these rings would be represented by the two beaded edges of the rim. But to obtain the required distribution of the lines of magnetic force the rings must be placed so that the magnetic force between them is one of *repulsion*; consequently the currents in these rings would be in opposite directions.

Whittaker has pointed out that the two ring electrons with opposed currents, described above, would be equivalent to a magnetic shell forming the curved surface of a cylinder, having its edges coincident with the two rings.

This model is open to the objection which Eldridge brought against the original model. With regard to such a suggestion Lorentz makes the comment: "It might seem at first sight that in a structure of this kind the magnets can be replaced by perfectly conducting solenoids carrying pre-existent electric currents, so that we can do without magnetic charges.

"In reality, however, no satisfactory model can be obtained in this way. This is seen most easily when the electron is supposed to move along the axis OX. In the magnetic field due to this motion the lines of force are circles around the axis, and therefore the line of force acting on an element of current at a point P is directed along a line lying in the plane POX. For such a point the moment with respect to OX is zero; consequently, neither a solenoid nor a system of solenoids can be acted on by a couple tending to produce a rotation about OX.

"Thus it would seem that the hypothesis of 'magnetism' existing independently of electric currents is quite essential to Whittaker's model. I need not speak at length of the reasons for which such an assumption is not to be readily admitted."

(2) In dealing with the transformation of energy into the radiant form Whittaker discards the magnetic wheel and deals with a Hertzian oscillator. It is important to notice that when he introduces a natural constant of action, he is departing from classical theory and postulating a vibrator which does not lead to the law of equipartition of energy.

At first sight Whittaker's choice of h/π as the value of the natural constant $e^2\sqrt{(L/C)}$ seemed somewhat arbitrary, and

of corresponding frequency. To make the comparison to a Hertzian oscillator valid, we must have the wheel execute angular oscillations, and this implies that when it is displaced from its initial position a restoring moment is called into being, so that the angular impulse which it receives as the electron passes through the system sets up oscillations like those of the balance wheel of a watch. The single line spectra of Franck and Hertz show that these oscillations are sensibly isochronous.

"In accounting for them it seems preferable not to drop the model at this stage. For in the model—as I have described it—there are essentially two magnetic systems in any atom: a centre one forming what is called the wheel, and another around it, which may for distinction be called the ring. (For simplicity of description we may confine the consideration to one plane. Thus



FIG. 15.—Ewing's Model.

in the figure we have a ring system ABCD as well as a wheel system W.)

"Each may be taken as rigid, but there is a freedom of relative rotation in the plane of the figure, except for the control exerted by magnetic forces between the two systems. These forces make the system take up a position of equilibrium as sketched, because the outer poles of the model have the same name as the inner poles of the ring. When an electron passes through and escapes it gives an impulse producing relative angular displacement. The mutual magnetic forces between the wheel and the ring tend to restore the whole to its original configuration. Thus oscillations are set up which expend their energy on the emitted radiation. In this form, therefore, the model furnishes a mechanism, not for extracting a quantum of energy, but for converting that into alternating magnetic currents and thereby into radiation."

It should be noticed that the electron gives angular momentum to the atom and itself loses only linear momentum along the axis. As Sir Alfred Ewing remarks : "The principle of conservation would seem to require the assistance of the æther." Again, on the basis of the model, the ejection of an electron from an atom gives the atom an angular impulse. This has a bearing on photo-electricity, and suggests the importance of considering circularly polarized light in our theoretical investigations of fundamental phenomena.

The question may be asked what is the relation between this model and that employed by Bohr. This question has been discussed by Whittaker, who has shown how it is possible in a formal way to assimilate to his own theory the part of Bohr's theory dealing with the transformation into monochromatic radiation of the energy set free by the fall of an electron from an outer to an inner orbit. In the next chapter we shall show that the quantum mechanism affords an opportunity of constructing a static model of an atom possessing many of the properties of the Bohr atom. But since the advent of the new wave-mechanics it is seen that it is no longer merely a choice between two alternative models, but a much wider problem involving a reconsideration of our ideas as to the nature of atomic systems and even of electric charges.

In concluding this account of the new mechanism suggested by Whittaker emphasis must be put on the essential point in his work, which is the "magnetic current." He says that it is simpler "to assume frankly that magnetic currents can exist in an atom, without laying stress on their realization by means of bar-magnets." And again, "the magnetic current is, in fact, a new conception ; and just because it is a new conception there must necessarily be some flaw in any attempt to represent it by means of old conceptions, such as bar-magnets."

CHAPTER IX

STATIC MODELS OF ATOMS AND MOLECULES

In ultimate logic any physical representation is in fact a mental construction or analogy, designed to relieve the mind from the intangible and elusive character of a complex of abstract relations.

LARMOR, *Aether and Matter*, p. 334, 1900

1. Some Advantages of Static Models

THE results of the X-ray analysis of crystals lend some support to the view that the electrons concerned in binding together the atoms of a metal in a crystal occupy more or less definite positions with reference to the atoms in the crystal lattice. In polar compounds such as rock salt (NaCl) the binding forces between the atoms can be regarded as due to the attraction of oppositely charged ions. The sodium ion resembles the neon atom, but possesses a nuclear charge of 11 instead of 10 units. The chlorine atom has one electron less than argon, but if it acquire an additional electron (say from a neutral sodium atom) it becomes a univalent chlorine ion, which resembles in its structure the argon atom. In the crystal of rock salt each sodium atom is surrounded by six chlorine atoms arranged symmetrically round it, and in the same way each chlorine atom is surrounded by six sodium atoms. We find, in fact, two interpenetrating face-centred cubic lattices. This may be interpreted by regarding the crystal as a pattern in three dimensions formed of sodium and chlorine ions of opposite signs, held together by electrostatic forces. According to W. H. and W. L. Bragg * the interatomic forces in metals may possibly be like those in polar compounds, the electrons playing the part of the negative ions. For example, metallic silver and silver chloride both have the same type of structure as rock salt, the length of the side of the elementary face-centred cube is in Ångström units 4.060 for the metal and 5.56 for the salt. This suggests that an electron in the metal takes the place of a chlorine ion in the salt.

It is of interest to note that in nearly all cases the lattice constant, i.e. the length of the side of the elementary cube or

* W. H. and W. L. Bragg, *X-rays and Crystal Structure*.

hexagon, is of the same order of magnitude for an element as for a polar compound. These results certainly suggest that the electrons occupy, or oscillate about, positions of equilibrium in the atomic lattice.

This view forms the basis of the theory developed by Borelius * to account for the electric properties of the metals, a theory which leads to results in good agreement with experiment. On the ground of simplicity there is much to be said for the supposition that the electrons concerned in fixing the space lattice of the metallic crystal are either stationary or execute small oscillations, and if this be correct, it is natural to assume that in a gaseous molecule also those electrons which play the part of chemical bonds occupy more or less fixed positions with regard to the atomic cores.

The question suggests itself whether it is possible to construct a static model of an atom in which *all* the negative electrons are in fixed positions with reference to the positive part of the atom. Historically, the atomic models of Kelvin and J. J. Thomson in which the positive electricity is a spherical volume distribution are of great importance, but when we employ the model of the nuclear atom the conditions for statical equilibrium cannot be satisfied in so simple a manner.

An interesting attempt to construct an atomic model on mechanistic principles was made in 1915 by A. L. Parson,† who supposed the electron endowed with a magnetic moment. A prominent feature of this theory is the group of 8 magnetons, which forms a system of low magnetic energy, and therefore of considerable stability. In the hydrogen molecule two shared magnetons are regarded as forming the chemical bond between two like atoms.

2. The Static Models of Lewis and Langmuir

A most interesting attempt to assign a definite spatial configuration to the electronic system of atoms and molecules has been made by G. N. Lewis, and his work has been extended by Langmuir. The facts of stereochemistry make it clear that an arrangement in three dimensions is required.

The inert gases are the most stable of the elements. We infer that in these the electron configurations are the most stable possible, and are "complete"; in other elements the groupings are incomplete, and the activity of such elements is attributed

* Borelius, *Phil. Mag.*, vol. 40, p. 746, 1920.

† A. L. Parson, *Smithsonian Miscellaneous Collections*, vol. 65, No. 11, 1915.

to the tendency to conform as nearly as possible to the structure of the rare gases.

The most stable element of all is *helium* with two electrons. Each electron may be imagined as situated in one half of a complete shell (like a walnut shell) surrounding the nucleus. It is not necessary to regard the electrons as stationary, but for simplicity each may be thought of as occupying its average position. The grouping in pairs about a positive charge may be regarded as the first electronic ideal.

The next most stable element is *neon*, atomic number 10. It is assumed that as in helium, two electrons are near the nucleus. The remaining 8 arrange themselves in a second shell, four in either hemisphere. This arrangement of 8 electrons may be called an *octet*. Next to the balanced pair of electrons the octet is the most stable grouping.

The arrangement of the electrons in the other inert gases, argon, krypton, xenon and niton (radon), is indicated in the table on p. 74.

The stability and inactivity of these elements is attributed to the electrons being placed in the most ideal position for the production of a balanced system, so that there is a minimum field of external force.

The key to all chemical combination is found in the striving of all elements to become as nearly as possible like the inert gases.

According to Lewis chemical compounds may be divided broadly into two types—*polar* and *non-polar*. As an example of the former type we take lithium fluoride. The single electron in the outer shell of the lithium atom may be supposed to pass to the outer shell of the fluorine atom so as to complete the octet. We then have a positively charged lithium ion and a negatively charged fluorine ion, and the electrostatic attraction between these ions results in the formation of a molecule of lithium fluoride (Li F).

In chemical compounds of the second type no ionization need be involved, and the chemical bonds or valencies are determined by pairs of electrons. In the Lewis-Langmuir theory one electron held in common never holds two atoms together; two atoms held together by a single valency bond hold two electrons in common. This is illustrated by the case of the fluorine molecule (Fig. 16).

The double valency bond implies that four electrons are held conjointly by two atoms (Fig. 17).

If the *pair* of electrons be regarded as the most stable grouping of all, it may be, as Lewis and Langmuir suggest, that the pairs of electrons held in common by two atoms are drawn closer together by the (magnetic) attraction between them. The

implied conception that the electron behaves as a magneton is of special interest in the domain of optical activity.* Dextro-



FIG. 16.—The Single Bond.

and lævo-rotatory forms of a compound might then be represented as mirror images as in Fig. 18. The letters N and S in this

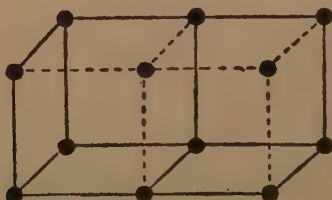


FIG. 17.—The Double Bond.

diagram may be taken to represent the polarity of the external face of the magneton.

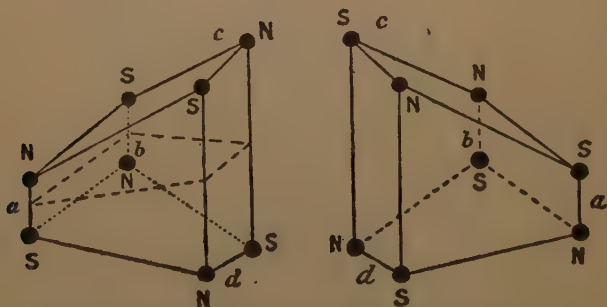


FIG. 18.—Optically active Forms of a Compound.

This view seems to give exactly the same number of isomerides as the ordinary structural formulæ. It is true that it is possible to reverse *in the diagram* the magnetic polarity of one or more

* H. S. Allen, *Nature*, vol. 105, p. 71, 1920.

pairs of electrons, but even if the arrangements so obtained were stable, it is doubtful whether they would represent different isomerides. It would not be possible to explain the phenomenon of free mobility about a single bond which is assumed in stereochemistry if such a reversal of the magnetic axis were accompanied by a change in the nature of the compound. Such modifications, however, might conceivably account for mutarotation.

The view here suggested appears to afford an adequate basis for a theory of optical activity. Such activity arises from a difference effect, and can be manifested only when there is lack of compensation amongst the electrons associated with the various parts of the molecule. If the chemical bond is to be attributed to a *pair* of electrons, it is easy to understand how such compensation can be brought about in the great majority of chemical compounds. In the case of a single asymmetric carbon atom, the symmetrical arrangement of each of the four electron pairs is disturbed by the presence of the adjacent groups, resulting in only partial compensation. Thus in the atom $a\ b\ c\ d$ (Fig. 18), the pair of electrons associated with group a is under the influence of the unlike groups c and d , and, therefore, cannot be symmetrical. But if c and d are made alike, the whole molecule will have a plane of symmetry indicated by the broken line in the left half of Fig. 18. Thus the molecule will be inactive through "internal compensation" with respect to the electrons which form the outer shell of the carbon atom. It may be added that the magnetic electron constrained to move backwards and forwards along its linear axis, is admirably adapted to replace the ordinary electron moving backwards and forwards along a spiral path postulated in Drude's theory of rotatory liquids.*

3. Mathematical Description of the Quantum Force

The success attained by the dynamic atom model of Bohr in the simpler atoms, especially in connection with spectroscopic deductions, is somewhat less marked in the more complex atoms, and when we turn to the question of chemical combination "we find that no satisfactory model of even the simplest *molecule*, that of hydrogen, has so far been constructed." †

Sir Joseph Thomson has done much to bridge the gap between chemistry and physics by attempting to extend the electronic theory of matter so as to explain how atoms may be linked together to form the stable system which constitutes a molecule. To avoid the difficulties inherent in the view that the electrons are

* H. S. Allen, *Phil. Mag.*, vol. 40, p. 426, 1920.

† Andrade, *The Structure of the Atom*, Chapter XII.

describing orbits under forces varying rigorously as the inverse square of the distance, he assumes that the electrons take up definite equilibrium positions under their mutual repulsions and forces exerted by the positive charges. Equilibrium is secured by postulating in the latter case a more complicated law of force than the inverse square, so that the attraction between an electron and a positive charge changes to repulsion at a certain distance. In particular he considers the case in which the force due to the central charge, E , is proportional to $\frac{E}{r^2} \left(1 - \frac{C}{r} \right)$. The first term

corresponds to the ordinary electrostatic force; the second term implies a force varying inversely as the cube of the distance. This is equivalent to assuming a repulsion, varying inversely as the cube of the distance, superposed on the ordinary attraction which varies inversely as the square of the distance. In this case attraction changes to repulsion when $r = C$.

Thus in the hydrogen atom the single electron will take up a position of stable equilibrium at a point where the attraction balances the repulsion; if the electron is displaced from this position in a direction away from the positive charge the force becomes attractive, and if it is displaced in the opposite direction the force becomes repulsive.*

Assuming a law of force of the form suggested, the potential energies of some atomic models have been calculated by Ida Woodward.† She has assumed further that two of the electrons are situated so near to the nucleus that in estimating the effect of the central charge they may be included in E . The number of external electrons considered is from 1 to 8, 12, 22 and 27. In the more complex cases several possible arrangements of the electrons are dealt with.

The law of force here postulated may be adjusted to meet the requirements of the quantum theory.

Langmuir ‡ has shown that a model of a static hydrogen atom may be obtained possessing many of the properties of the Bohr atom with its circling electrons, if it be assumed that in addition to the Coulomb force between charged particles there exists another force given by

$$F = \frac{1}{mr^3} \left(\frac{nh}{2\pi} \right)^2 \quad \dots \dots \dots 9:1$$

acting between an electron (mass m , charge e) and a nucleus. In the formula n is an integer, and h is Planck's constant. By assigning various values to n a series of definite equilibrium

* J. J. Thomson, *Phil. Mag.*, vol. 41, p. 510, 1921.

† Ida Woodward, *Phil. Mag.*, vol. 47, pp. 992-1016, 1924.

‡ Langmuir, *Phys. Rev.*, vol. 18, p. 104, 1921.

In work connected with atomic or molecular structure it is convenient to express all lengths in terms of a_n . If we do this we find that the "quantum force" may be expressed very conveniently in the form

$$F = e^2 \cdot \frac{a_n}{r^3} \quad . \quad . \quad . \quad . \quad 9:7$$

This form of the expression suggests that in addition to the ordinary electrostatic force, e^2/r^2 , between elementary charges (a force which is attractive for opposite charges, repulsive for similar charges) there may be this "quantum force," $e^2 a_n/r^3$ *which is repulsive for unlike charges, but attractive for like charges*. It must be pointed out that the force postulated by Langmuir is assumed to act along the line joining two charged particles. It is possible, and even probable, that closer correspondence between theory and experiment would be obtained by assuming a variation in the magnitude of the quantum force with the direction, as is indeed suggested by the quantum mechanism devised by Whittaker.

The relation between the static atom of Langmuir and the dynamic atom of Bohr has been treated from the mathematical standpoint by G. C. Evans * who has discussed the question of reality and preference in terms of transference processes, which may carry one system into the other. He concludes as follows: "Two models of the atom must be regarded as equivalent, or equally real, if each has all the energy levels of the other in the presence of the same phenomena, such as radiation, Zeeman effect, Stark effect, compression, etc. For there is then no way that one may be distinguished from another by means of these phenomena. That sort of indefiniteness is a characteristic of the quantized system.

"It is entirely legitimate for the physicist to consider the atom as a Bohr atom for the phenomena of radiation, and as a Langmuir atom in the presence of chemical phenomena, the transformation from one to the other being imagined as an actual mechanical process. Such a process may be called a transference process."

Langmuir's quantum force has been employed in discussing static models for the hydrogen molecule and also for the atom and molecule of helium.

4. A Static Model for the Hydrogen Molecule

Before describing the static model for the hydrogen molecule we shall, for the sake of comparison, briefly refer to the dynamic model of Bohr.

* G. C. Evans, *Nat. Acad. Sci. Proc.*, vol. 9, pp. 230-6, 1923.

In this model the two electrons move in circular orbits in a plane bisecting at right angles the line joining the hydrogen nuclei. The electrons, which are always at opposite ends of a diameter of the circle, have each an amount of angular momentum, $nh/2\pi$.

In its most stable form Bohr's model is represented in Fig. 19,

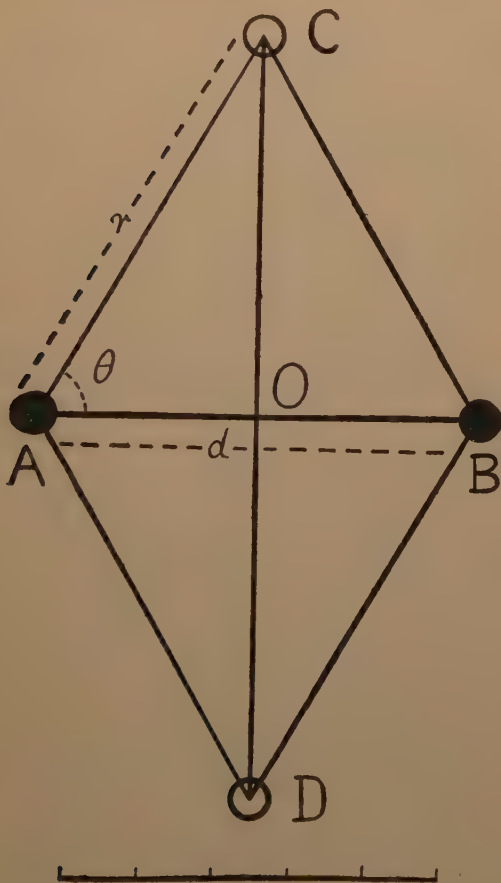


FIG. 19.—Hydrogen Molecule, $\theta = 60^\circ$.

the black circles representing the protons and the white circles the electrons. It is easy to show that each electron must be at the vertex of an equilateral triangle, having as its base the line joining the protons.

It is possible to replace Bohr's model with its revolving electrons by a model in which the electrons occupy positions of

equilibrium with respect to the hydrogen nuclei provided we introduce Langmuir's quantum force between each pair of four electric charges which constitute the neutral hydrogen molecule.*

Considering only symmetrical arrangements we may denote by θ the angle between the line joining the two nuclei and the line drawn from the nucleus to an electron. We find that there

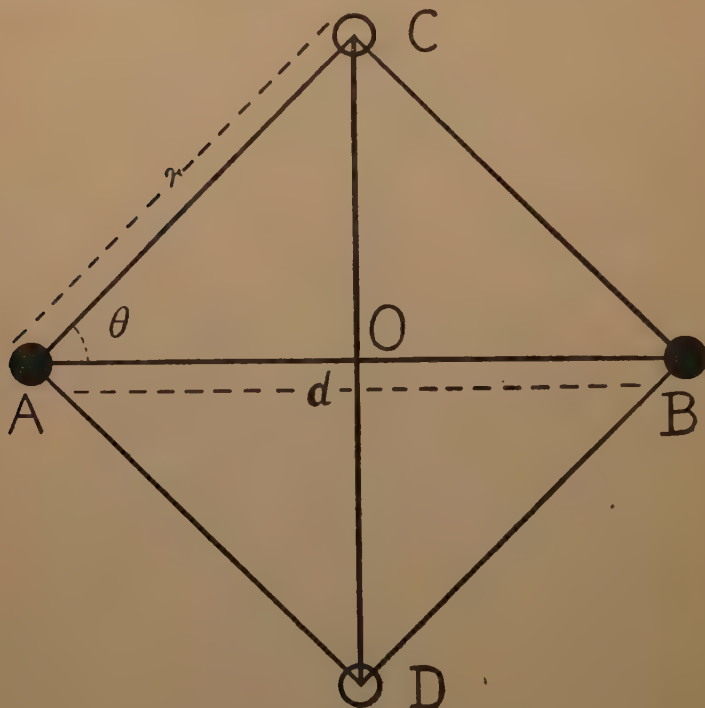


FIG. 20.—Hydrogen Molecule, $\theta = 45^\circ$.

are three possible values for θ , which may be 45° , 60° or 30° giving three possible configurations for the molecule.

The most stable configuration from the point of view of ordinary statics appears to be that in which the nuclei and electrons are situated at the corners of a square, with the nuclei at the ends of one diagonal and the electrons at the ends of the other. The length of a diagonal is $1.641 a_n$. When $n = 1$, the length of a diagonal is 0.871 A.U., and this case is illustrated in Fig. 20. Another configuration agrees exactly with that obtained

* H. S. Allen, *Roy. Soc. Edin. Proc.*, vol. 43, p. 180, 1923.

from Bohr's theory and is shown in Fig. 19, but the electrons are now at rest instead of in orbital motion. In the third configuration, the positions of the charges are similar to those shown in Fig. 19, but the black and white circles must be interchanged.

DATA FOR HYDROGEN MOLECULE

	θ	$d(\text{\AA})$	$I \times 10^{41}$	W (volts)
Neutral hydrogen molecule	45°	0.871	0.261	30.06
	60°	0.5845	2.818	29.68
	30°	1.012	8.453	29.68
Ionized Molecule		1.239	12.66	17.34
Triatomic Molecule		—	9.726 19.452	46.25

In the table the values in the second row correspond to Bohr's model.

Some of the data relating to the neutral molecule are collected in the previous table, Bohr's values coinciding with those for $\theta = 60^\circ$. The distance, d , between the protons is given in Ångström Units, the moment of inertia I in C.G.S. units and the value of W , the work required for complete dissociation, in equivalent volts.

The actual existence of a positively charged hydrogen molecule has been demonstrated experimentally.

On the basis of the present theory a static model may be obtained in which a single electron is placed midway between two positively charged nuclei, and data for this model are given in the table. The calculated ionization potentials are in moderately good agreement with the experimental results, but the model cannot be said to give exact agreement.

From observations of positive-ray parabolas corresponding to mass 3, Sir Joseph Thomson* came to the conclusion that triatomic hydrogen, H_3 , existed in his discharge tubes. Chemical workers have prepared this substance by several different methods and have found that the molecule contains three hydrogen atoms. A more conclusive proof of the existence of triatomic hydrogen has been given by Aston by means of the mass-spectrograph.

The author has suggested a possible configuration of a symmetrical character for the neutral molecule in the form of a hexagon with three hydrogen nuclei and three electrons in the alternate corners. This configuration may be investigated in terms of Langmuir's quantum force, and we then obtain the

* J. J. Thomson, *Rays of Positive Electricity*, p. 196 (1921).

results given in the table. It may be pointed out that the method would also lead to unsymmetrical configurations which would yield different values for the characteristic constants.

It is of interest to note that from a study of the secondary spectrum of hydrogen at higher pressures, Sandeman* has isolated a band, showing a P, Q, and R combination having a moment of inertia agreeing within the errors of measurement with that found for this static model of triatomic hydrogen.

5. A Static Model for Helium

For the positively charged helium atom,† consisting of a positively charged nucleus (charge $+2e$) and a single negative electron (charge $-e$), there is a position of stable equilibrium determined by $r = \frac{1}{2}a_n$. The work that must be done to remove the electron from this position to a position of rest at an infinite distance from the nucleus is four times the corresponding amount in the case of the hydrogen atom, exactly as in Bohr's original theory. It is assumed that there is repulsion between nucleus and electron due to the quantum force, of amount e^2a_n/r^3 .

For a neutral helium atom, consisting of a positive nucleus and two electrons, a number of configurations are theoretically possible. We consider first symmetrical configurations in which the nucleus is at the middle point of the line joining the electrons. The table below gives the results for two possible models, A and B. A refers to a model in which *no* quantum force acts between the electrons, and B to a model in which such a force is included.

DATA FOR HELIUM ATOM

	r (A.U.)	W (volts)
Ionized helium atom, C	0.265	54.10
Neutral helium atom, A	0.303	82.84
Neutral helium atom, B	0.265	94.67
Change from A to C	—	28.74
Change from B to C	—	40.57

These values of W for the neutral atom are not in agreement with the experimental results, which yield the value 78.6 volts. If, however, we assume with Bohr that a neutral atom is formed by the successive binding of electrons by the atomic nucleus, it may be that the symmetrical arrangement assumed is never

* Sandeman, *Proc. Roy. Soc.*, vol. 108, p. 607, 1925.

† H. S. Allen, *Proc. Roy. Soc. Edin.*, vol. 44, p. 116, 1924.

realized. A number of asymmetrical configurations of the helium atom have been worked out, but none of the cases considered gives exact agreement with the experimental value, the nearest approach being 77.26 volts, this value involving the use of half-quantum numbers.

The existence of a helium molecule is required for the explanation of the band spectrum, though no doubt the molecule is unstable and only has a transitory existence. The moment of inertia calculated is of the same order of magnitude as that determined by Curtis from observations of the band spectrum.

We may conclude that although the static models here considered may not possess all the advantages possessed by the dynamic models, they may be usefully employed for certain purposes owing to the comparative simplicity of the mathematical processes and the physical conceptions involved.

CHAPTER X

QUANTUM TUBES OF MAGNETIC INDUCTION

" Si les trajectoires de Bohr n'émettent aucune onde leurs champs à grande distance doivent être constants. . . . Les quanta ont donc pour effet de produire à une certaine distance de l'atome un régime permanent, une organisation des lignes de force en tubes invariable, analogues à des tourbillons stationnaires en hydrodynamique. Les conclusions ont une importance particulière au point de vue de notre conceptions du champ magnétique. Dans la théorie de la relativité, ce dernier ne se distingue pas essentiellement du champ électrique ; il se comporte en gros comme un vecteur auxiliaire. La théorie des quanta lui rend une réalité physique propre, elle nous conduit à imaginer des tubes d'induction stable multiples d'un tube unité correspondant au magnéton."

E. BAUER, C.R., vol. 174, pp. 1335-1338, May 22, 1922

1. Magnetic Tubes threading a Circular Orbit

IN Chapter III it was suggested that the atomicity demanded by the quantum theory is connected with the existence of discrete tubes of magnetic induction, the unit tube being determined by the ratio of Planck's constant to the electron charge. We now proceed to consider how this view (which was derived by assuming that the electron possessed not only an electric charge but also a magnetic moment) may be associated with Bohr's conception of a classical electron in a stationary state of orbital motion.

It seems probable that the result previously obtained as to the number of magnetic tubes threading the aperture of a ring electron may be applied also to the case of a classical electron circulating in a closed orbit. Such an extension has in fact been suggested in an interesting paper by A. L. Bernoulli * published in 1916. This author has given an electrodynamic interpretation of Planck's constant by introducing a principle which he terms the " Principle of the Universal Flux of Induction." The principle is defined as follows: " If electrons are moving in

* A. L. Bernoulli, *Archives des Sciences*, vol. 42, p. 24, 1916.

Thus, as we found previously in dealing with the ring electron, the number of magnetic tubes is $n\left(\frac{h}{e}\right)$, and is an integral number of times the constant quantity h/e , which we take to define the unit quantum tube.

It may be pointed out that here, as in the electronic theory of magnetism developed by Langevin, it is assumed that the classical electron circulates with very high frequency, and may be treated as equivalent to a continuous current giving rise to a magnetic field similar to that produced by a steady current.

In a paper read before the Royal Society of Edinburgh in 1921 the author * gave a more general proof of the principle of Bernoulli, with the object of avoiding as far as possible particular assumptions as to the character of the electrical distribution. A system was considered composed of a number of point charges rotating about an axis with the same uniform angular velocity, ω .

Although the model employed may differ widely from an actual atomic or molecular system, the method of calculating the angular momentum is of some interest and will now be indicated.

The equivalent mass per unit volume of an electrostatic tube is $4\pi\mu D^2 \sin^2\theta$, where D is the electric polarization or displacement, and θ is the angle between the direction of the tube and its velocity. Hence the angular momentum for unit volume of the tube is $(4\pi\mu D^2 \sin^2\theta)r^2\omega$. The moving Faraday tubes are accompanied by a magnetic field, at right angles to their length and to their direction of motion, given by $H = (4\pi D \sin\theta)r\omega$. Hence $(D \sin\theta)r = H/4\pi\omega$, and the angular momentum for unit volume of the tube may be written

$$4\pi\mu\omega\left(\frac{H}{4\pi\omega}\right)^2 = \frac{2}{\omega} \times \frac{\mu H^2}{8\pi} \quad \dots \quad 10:7$$

Hence the total angular momentum of the system takes the form $\frac{2}{\omega} \sum \frac{\mu H^2}{8\pi}$, the summation extending over the whole space occupied by the magnetic tubes.

The sum $\sum \frac{\mu H^2}{8\pi}$ represents the electrokinetic energy, and may be expressed in the form $\frac{1}{2}L_1 i_1^2 + \dots + M_{12} i_1 i_2 + \dots$, where L_1 is the self inductance for the circuit carrying a current $i_1 = \frac{e_1 \omega}{2\pi}$, M_{12} the mutual inductance for the circuits i_1, i_2 , etc.

* H. S. Allen, *Proc. Roy. Soc. Edin.*, vol. 41, p. 34, 1921.

2. Magnetic Tubes threading an Elliptic Orbit

In the earliest form of Bohr's theory circular orbits only were considered, but as we have seen it became necessary to take into account more complicated orbits and of these the next in order of simplicity is the Keplerian ellipse. The quantized elliptic orbit is discussed in Appendix IV, p. 259. The author * has investigated the number of quantum magnetic tubes linked with such an orbit, and the result will here be briefly stated. The size and shape of an elliptic orbit depend on two integers, n_ϕ , the azimuthal quantum number, and n_r , the radial quantum number. It is found that the sum of these integers $n_\phi + n_r$,

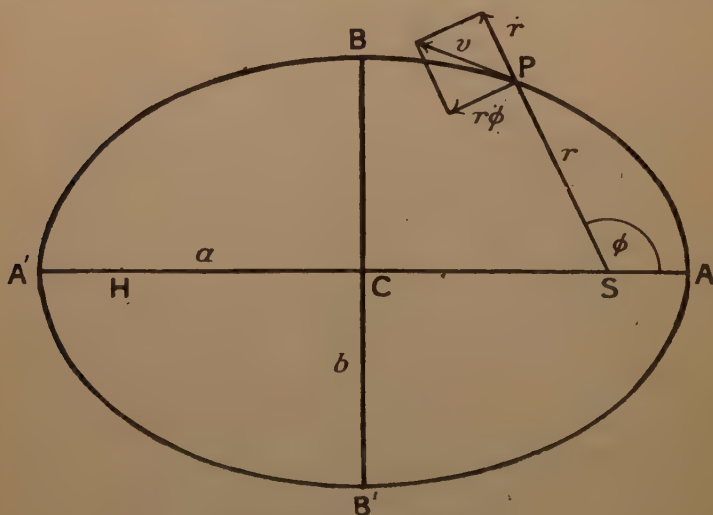


FIG. 21.—Elliptic Orbit.

which is equal to the "principal quantum number," n , of Bohr represents the number of quantum magnetic tubes passing through the elliptic orbit.

We take r, ϕ as the polar co-ordinates of the electron with the focus as origin. Corresponding to the angular motion in ϕ there is an amount of angular momentum, $mr^2\dot{\phi}$, which in this case is constant and may be represented by $\dot{\phi}$.

The quantum relation (see Appendix IV, equation 10) for the azimuthal motion may be written in the equivalent forms

$$\oint p dq = p \int_0^{2\pi} d\phi = 2\pi p = n_\phi h, \text{ or}$$

$$\oint mr^2 \dot{\phi} d\phi = \oint mr^2 \dot{\phi}^2 dt = n_\phi h \quad . \quad . \quad . \quad 10:13$$

* H. S. Allen, *Phil. Mag.*, vol. 42, p. 523, 1921.

If we regard the angular momentum of the revolving electron as the angular momentum of moving Faraday tubes, as we did in the case of a circular orbit, it is easy to show by just the same method we employed before, that the angular momentum may be written as

$$\frac{2}{\phi} \Sigma \frac{\mu H^2}{8\pi}.$$

This summation extends over the whole space occupied by magnetic tubes at the particular instant which we are considering. Consequently

$$\frac{2}{\phi} \frac{\Sigma \mu H^2}{8\pi} = p \quad . \quad . \quad . \quad . \quad 10 : 14$$

where p is the constant value of the angular momentum. We see, then, that the sum

$$\frac{\Sigma \mu H^2}{8\pi} = \frac{1}{2} p \phi \quad . \quad . \quad . \quad . \quad . \quad 10:15$$

Now this sum represents the *instantaneous* value of the electrokinetic energy. We can determine the *average* value of the electrokinetic energy in one revolution, or the average value of $\frac{1}{2}p\phi$, and we find

$\phi\pi\nu$ or $\frac{1}{2}n_{\phi}h\nu$ 10:16

But another way of expressing the electrokinetic energy is in terms of the magnetic lines threading a current circuit. If we have a current, i , flowing round a circuit, and there are N lines threading through the circuit, the electrokinetic energy will be $\frac{1}{2}Ni$. If we identify this expression $\frac{1}{2}Ni$ with $\frac{1}{2}n_{\phi}h\nu$, we find on putting $i = ev$

$$N = n_{\phi} \left(\frac{h}{e} \right) \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad 10:17$$

that is to say, the number of magnetic tubes threading the circuit and corresponding to the angular motion is an integral number of times $\left(\frac{h}{e}\right)$, the integer being the azimuthal quantum number n_ϕ .

The radial quantum motion may be treated in the same way

$$\phi p_r dr = \phi m r dr = \phi m r^2 dt = n_r h \quad . \quad . \quad 10:18$$

Here mv^2 is equal to twice the instantaneous value of that part of the kinetic energy which depends on the radial motion. But we have to integrate that instantaneous value with regard to the time, so the quantum equation expresses the fact that

$$\frac{2 \text{ (Average value of kinetic energy)}}{\nu} = n_f h,$$

The simplicity of the final result suggests that it may be reached by a shorter path. In Appendix IV it is shown that the value of Bohr's W for an elliptic orbit is given by

$$W = \frac{1}{2}(n_\phi + n_r)h\bar{\nu} \quad . \quad . \quad . \quad . \quad 10:21$$

where $\bar{\nu}$ is the frequency of the electron in its orbit.

Let us now assume that the numerical value of W may be identified with the electrokinetic energy of the field of the revolving electron. The electrokinetic energy may be expressed as

$$\frac{1}{2}Ni = \frac{1}{2}Ne\bar{\nu} \quad . \quad . \quad . \quad . \quad 10:22$$

and when we identify these two expressions we find that

$$N = (n_\phi + n_r)(h/e) \quad . \quad . \quad . \quad . \quad 10:23$$

so that the total number of magnetic tubes threading through the elliptic orbit is determined by the sum of the two integers n_ϕ and n_r .

All the results obtained in considering the elliptic orbit are consistent with one another, because they are all based on the same set of assumptions. Although this investigation cannot be regarded as furnishing a definite proof of the existence of discrete tubes of magnetic induction, it affords strong presumption of the existence of physical entities of this kind. We must, however, be prepared to revise our conception of what constitutes a physical entity in the light of the theory of relativity.

3. Quantum Magnetic Tubes for two Current Circuits

It has been shown previously that when a charge, e , is moving in an orbit of any shape whatever with high frequency ν , there is associated with each canonical co-ordinate a magnetic flux of an integral number of magnetic tubes, the unit tube being defined by the ratio h/e , where h is Planck's constant. There is a magnetic flux through the orbit which may be considered as constituted by a definite whole number of discrete magnetic tubes defined as above.

We now proceed to consider more complex distributions. As a typical case we take two current circuits, carrying currents i_1 and i_2 respectively. These circuits may be regarded as representing two magnetons or two electron orbits.

Let L_1 = the self inductance of the first circuit.

L_2 = the self inductance of the second circuit.

M_{12} = the mutual inductance of the two circuits.

Defining magnetic tubes in the way customary in electromagnetic theory

$L_1 i_1$ = the number of magnetic tubes threading through circuit No. 1 due to its own current.

$L_2 i_2$ = the corresponding number of tubes for circuit No. 2.

$M_{12} i_1$ = the number of tubes threading through circuit No. 2 due to the current in circuit No. 1.

$M_{12} i_2$ = the number of tubes threading through circuit No. 1 due to the current in circuit No. 2.

The magnetic tubes may be grouped together in various different ways which may be illustrated more clearly by a purely diagrammatic scheme such as that illustrated in Fig. 22.

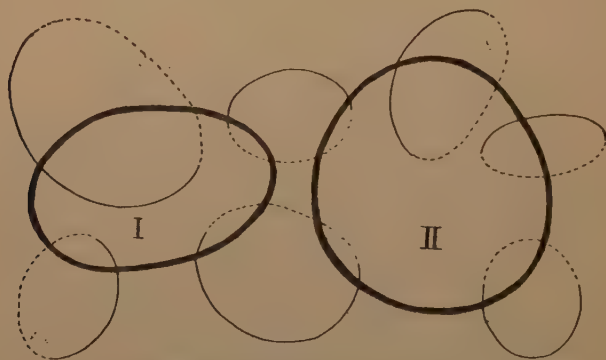


FIG. 22.—Magnetic Tubes for two Current Circuits.

The two current circuits I and II are shown in black. In this case

N_1 , the number of tubes linked only with circuit I is 2,

N_2 , the number of tubes linked only with circuit II is 3,

N_{12} , the number of tubes linked with both circuits is 2,

n_1 , the total number of tubes linked with circuit I is 4,

n_2 , the total number of tubes linked with circuit II is 5,

whilst the total number of tubes in the diagram is 7.

The *total* number of tubes linked with the first circuit is

$$n_1 = L_1 i_1 + M_{12} i_2 \quad . \quad . \quad (4 \text{ in Fig. 22})$$

The *total* number of tubes linked with the second circuit is

$$n_2 = L_2 i_2 + M_{12} i_1 \quad . \quad . \quad (5 \text{ in Fig. 22})$$

Again, the number, N_1 , of tubes linked *only* with circuit No. 1 is the difference between the number of tubes passing through circuit No. 1 due to its own current, and the number passing through circuit No. 2 due to the current in circuit No. 1, i.e.

$$N_1 = L_1 i_1 - M_{12} i_1 \quad . \quad . \quad (2 \text{ in Fig. 22})$$

In the same way the number of tubes linked *only* with circuit No. 2 is

$$N_2 = L_2 i_2 - M_{12} i_2 \quad . \quad . \quad (3 \text{ in Fig. 22})$$

Last of all we have tubes linked with *both* circuits and the number of these is

$$N_{12} = M_{12}(i_1 + i_2) \quad . \quad . \quad (2 \text{ in Fig. 22})$$

The *total* number of tubes is obviously

$$N_1 + N_2 + N_{12} = L_1 i_1 + L_2 i_2 \quad (7 \text{ in Fig. 22})$$

a result which we might have foreseen.

The simple fact, illustrated in Fig. 22, that the various magnetic tubes associated with two current circuits, may be grouped together in different ways, is important in connection with the method of applying the quantum conditions. In his original work the author * started by classifying the tubes by the latter method, i.e. by considering the tubes linked *only* with either circuit. It is, however, more satisfactory to adopt the former classification and consider the *total* number of tubes linked with each circuit. The reason is that we are then able to apply the quantum conditions according to the accepted principles in the way suggested by Professor C. G. Darwin of the University of Edinburgh. His treatment, with slight alterations in the notation, is given below.

We are dealing with a system depending upon two variables which in this case might be taken as the two currents i_1 and i_2 , but we may start by attempting to quantize the general expression

$$W = \frac{1}{2} a \dot{x}^2 + f \dot{x} \dot{y} + \frac{1}{2} b \dot{y}^2 \quad . \quad . \quad . \quad 10 : 24$$

This is a quadratic function of the variables $\dot{x}$ and $\dot{y}$ which are supposed to have the same periodic character, and the cycles for $\dot{x}$ and $\dot{y}$ are supposed to be from 0 to 1. In accordance with the Hamiltonian method previously discussed we put

$$\left. \begin{aligned} p_x &= a\dot{x} + f\dot{y} \\ p_y &= f\dot{x} + b\dot{y} \end{aligned} \right\} \quad . \quad . \quad . \quad 10 : 25$$

Making the substitution we find

$$W = \frac{1}{2} \frac{b p_x^2 - 2 f p_x p_y + a p_y^2}{ab - f^2} \quad . \quad . \quad . \quad 10 : 26$$

Then the motion is determined by the Hamiltonian equations

$$\frac{dp_x}{dt} = -\frac{\partial W}{\partial x} = 0, \text{ etc.}, \quad \dot{x} = \frac{\partial W}{\partial p_x}, \text{ etc.} \quad . \quad . \quad 10 : 27$$

This gives

$$p_x = \text{constant} \quad . \quad . \quad . \quad 10 : 28$$

If, then, we apply the quantum condition as given by Wilson and Sommerfeld (2 : 18) we have an integral taken over a cycle represented by

$$\oint p_x dx = \tau_1 h, \text{ etc.}, \text{ where } \tau_1 \text{ is an integer} \quad . \quad 10 : 29$$

* H. S. Allen, *Phil. Mag.*, vol. 48, p. 429, 1924.

Since $\dot{p}_x = \text{constant}$ and the x cycle is from 0 to 1, we get

$$\dot{p}_x = \tau_1 h, \text{ etc.} \quad \dots \quad 10:30$$

If we substitute this expression in the value for W , the latter takes the form

$$W = \frac{1}{2} h^2 \frac{b\tau_1^2 - 2f\tau_1\tau_2 + a\tau_2^2}{ab - f^2} \quad \dots \quad 10:31$$

Now let us seek to use this method for the two current circuits. The expression for the electrokinetic energy for two current circuits is

$$W = \frac{1}{2} L_1 i_1^2 + M_{12} i_1 i_2 + \frac{1}{2} L_2 i_2^2 \quad \dots \quad 10:32$$

This expression is of the form used in equation 10:24, but we notice that when we take $\oint \dot{p} di$ for a complete period the result corresponds to an electric charge, and must be capable of expression as an integral multiple of the fundamental electron charge, i.e. $\oint \dot{p} di = \kappa e$ where κ is an integer. When we apply the quantum conditions, we find that

$$\left. \begin{aligned} \kappa_1 e (L_1 i_1 + M_{12} i_2) &= \tau_1 h \\ \kappa_2 e (M_{12} i_1 + L_2 i_2) &= \tau_2 h \end{aligned} \right\} \quad \dots \quad 10:33$$

Employing the results on page 142, we find the *total* number of quantum tubes linked with a circuit given by

$$\left. \begin{aligned} \kappa_1 e n_1 &= \tau_1 h \\ \kappa_2 e n_2 &= \tau_2 h \end{aligned} \right\} \quad \dots \quad 10:34$$

and so

$$\left. \begin{aligned} n_1 &= \frac{\tau_1}{\kappa_1} \left(\frac{h}{e} \right) \\ n_2 &= \frac{\tau_2}{\kappa_2} \left(\frac{h}{e} \right) \end{aligned} \right\} \quad \dots \quad 10:35$$

As in our previous work, the simplest interpretation of these results is to assume the existence of discrete quantum tubes of magnetic induction, the unit tube being defined by h/e . That is to say, the integer κ_1 may be supposed to divide exactly into the integer τ_1 , and κ_2 divide exactly into τ_2 .

The suggested existence of half-quanta may represent a case where these integers will not divide exactly.

In concluding the discussion of the case of two current circuits, attention may be directed to a mechanical model * representing the behaviour of two such circuits, constructed on the lines of a model due to Clerk Maxwell (1876). It has been found possible to make a model showing very close analogy to the electrical system and suggestive in dealing with the present problem.

* H. S. Allen, *Phil. Mag.*, vol. 48, p. 429, 1924.

We now *assume* that the quantum condition may be expressed in the form

$$2 \int T dt = nh \quad . \quad . \quad . \quad . \quad 10:40$$

where n is an integer. Then we can write

$$\mu HA \int (i_1 + i_2 + i_3 + \dots + i_n) dt = nh \quad . \quad 10:41$$

assuming that in each part of the integral the integration extends over a period corresponding to a particular current.

This is an arbitrary way of stating the quantum conditions, but so is any statement of these conditions, which must be regarded rather as a set of rules justified by the results obtained than as a consistent and unique theory.

Now $\int i_1 dt$ when the integration extends over a corresponding period, will represent the charge, and assuming the charge to be built up of electronic units, it must take the form $\kappa_1 e$. Treating the other terms in the same way, we get

$$\mu HA (\kappa_1 + \kappa_2 + \dots + \kappa_n) e = nh \quad . \quad . \quad 10:42$$

The simplest interpretation of this result is to assume, as we have done in previous cases, that the sum of the integers is equal to n or is some sub-multiple of n . That means that the unit tube is defined by $(\mu HA) e = h$ or $\mu HA = h/e$.

Next consider the electrokinetic energy of the unit quantum tube in question. This is given by

$$\begin{aligned} & \frac{1}{2} \mu HA (i_1 + i_2 + i_3 + \dots + i_n) \\ &= \frac{h}{2} (\kappa_1 \nu_1 + \kappa_2 \nu_2 + \dots + \kappa_n \nu_n) e \quad . \quad . \quad 10:43 \end{aligned}$$

since i_1 , the current in the first circuit, may be expressed in the form

$$i_1 = \kappa_1 e \nu_1,$$

where ν_1 is the frequency in that orbit.

In most atomic systems it is probable that the integer represented by κ is unity in each case, and so the energy would reduce to

$$\frac{1}{2} h (\nu_1 + \nu_2 + \nu_3 + \dots + \nu_n) \quad . \quad . \quad . \quad 10:44$$

We see from this expression that the energy of the tube may be expressed in the typical form $\frac{1}{2} h \nu$, where ν is the frequency, which may be the result of adding algebraically a number of independent frequencies. We notice that ν is a frequency characteristic of the particular quantum tube under consideration.

It is tempting to suppose that it corresponds to the frequency of a state of spin or vorticity appropriate to that tube.

5. Application to the Theory of Spectral Series

It may be remarked that a prominent feature of Bohr's theory of spectral series is the fact that frequency plays the part of an additive quantity as it does in this expression for the energy of a quantum tube.

The *kinematical* significance of Bohr's equation $h\nu_r = W' - W$ may be realized by expressing W in the form $\frac{1}{2}nh\nu$. The frequency of the radiation emitted is then given by

$$h\nu_r = \frac{1}{2}n'h\nu' - \frac{1}{2}nh\nu \quad . \quad . \quad . \quad 10:45$$

This relation can be interpreted by taking the frequency ν_r of the emitted radiation as identical with a definite frequency associated with a quantum tube or tubes of magnetic induction, such frequency being one characteristic feature of the system, both in its initial and in its final state.

It has been shown that the integer n in the expression $W = \frac{1}{2}nh\nu$ may be interpreted as the total number of quantum tubes linked with the orbit of the electron, whether the orbit be a circle or an ellipse. Consequently, when, in Bohr's theory, a change takes place from one stationary state to another and n changes to n' , there is an integral change in the total number of tubes linked with the orbit. When radiation is *emitted* there is a *diminution* in the number of these tubes equal to $n - n'$. But it is assumed in the theory that, whatever may be the value of $n - n'$, only one quantum of radiation is emitted. On the view now suggested it is natural to suppose that the radiated energy is the energy associated with a single quantum tube, the emission of radiation being a process consisting in, or consequent upon, the liberation of one quantum tube from the atomic system. It is, however, only when the electron passes between neighbouring orbits that the diminution in the number of tubes, $n - n'$, is equal to unity. In general, the decrease in the number of tubes linked with the orbit is more than sufficient to account for the single tube we have supposed separated from the system. If, then, we regard magnetic tubes as entities which can change in form, but cannot be created or destroyed (so long, at least, as they are associated with an atomic system), we are forced to the conclusion that there must be some part of the system which can serve as a receptacle for the surplus tubes. Such a receptacle may be described as a "magneton," using that term in the wide sense advocated elsewhere* to denote

* H. S. Allen, *Proc. Roy. Soc. Edin.*, xlii., p. 213 (1922).

that structure within the atom which may be regarded as the origin of the quantum magnetic tubes.

Consider the case of an atom consisting of a positive core and a negative electron. There are two possibilities presenting themselves. The core of the atom may be a magneton, or the negative electron may be a magneton.

Without entering into a discussion of these alternatives, it will be sufficient for our present purpose to assume that the magneton is closely associated with an integral number of quantum tubes of frequency ν_r . As in Bohr's theory, the electron is supposed to describe an orbit about the nucleus, the size of the orbit and the frequency being determined by the usual quantum relations. For simplicity we shall consider the case of a massive nucleus, which may be regarded as at rest.

Let n denote the number of quantum tubes linked with the orbit and also passing through the magneton, and n_r the number of quantum tubes associated with the magneton which are not linked with the orbit.

Then, in accordance with the principles discussed in the earlier portion of this chapter, the electrokinetic energy of the system in its initial state is given by

$$T = \frac{1}{2}n_r h\nu_r + \frac{1}{2}nh(\nu + \nu_r) \quad . \quad . \quad . \quad 10:46$$

Denoting the corresponding quantities in the final state by accented letters, we have, similarly,

$$T' = \frac{1}{2}n_r' h\nu_r' + \frac{1}{2}n'h(\nu' + \nu_r') \quad . \quad . \quad . \quad 10:47$$

To proceed further we have to make some specific assumptions with regard to the frequencies. In the first place, we assume that the frequency ν_r remains unchanged in passing from the initial to the final state, and we identify this frequency with that of the emitted radiation.

In systems which emit hydrogen-like spectra the kinetic energy is numerically the same as Bohr's W . In his theory the kinetic energy in the new orbit is greater than that in the old, but the amount of potential energy set free is exactly twice the change in the kinetic energy. Consequently, an amount of energy is available for radiation which is equal to the change in the kinetic energy. This is

$$T' - T = \frac{1}{2}[(n_r' + n') - (n_r + n)]h\nu_r + \frac{1}{2}n'h\nu' - \frac{1}{2}nh\nu \quad 10:48$$

We now assume that in the change from one state to the other *one* quantum tube has been liberated from the magneton, and put

$$\frac{1}{2}h\nu_r = T' - T \quad . \quad . \quad . \quad 10:49$$

Hence

$$\frac{1}{2}h\nu_r = \frac{1}{2}[(n_r' + n') - (n_r + n)]h\nu_r + \frac{1}{2}n'h\nu' - \frac{1}{2}nh\nu \quad 10:50$$

But if a single quantum tube is liberated, the total number of bound tubes in the initial state is one greater than the total number in the final state, i.e.

$$n_r + n = n_r' + n' + 1 \quad . \quad . \quad . \quad 10:51$$

Thus the above equation reduces to

$$h\nu_r = \frac{1}{2}n'h\nu' - \frac{1}{2}nh\nu \quad . \quad . \quad . \quad 10:45$$

which is identical with that employed by Bohr.

6. The Fundamental Nature of Magnetic Lines

A few remarks may be added with regard to the general character of magnetic lines, as bearing on what has been said. Sir Oliver Lodge in various papers has referred to the fundamental character of such lines.

“How then are we to visualize the act of magnetization, say, when a piece of iron is magnetized? I say that the act consists in opening out molecular magnetic loops which are already in existence. They are like rings swelling sideways. You cannot cut them or get at their ends, as you can cut a loop of string. They are more like indiarubber bands which can be stretched, stretched without limit; so that, instead of being shut up into an ultra-microscopic space, they swell out so as to enclose a considerable region. The lines of force of an active magnet envelop a large area, and when the magnetism is destroyed or suppressed, the loops do not cease to be, they merely shrink, so as to enclose a smaller and smaller area as the magnetism dies away; and they remain, ready to be swollen out again when the magnetism is re-excited.”*

“Magnetic lines are always closed curves; there is no known way of generating them, they always pre-exist, though they may be of atomic or molecular magnitude, and in a magnetic field are opened out so as to enclose a perceptible area. This is generally admitted to be the process of magnetization, and when the magnetism ceases the lines shrink up into infinitesimal, or practically infinitesimal, orbits again. That the *quantum* is associated with these ultimate magnetic units is exceedingly likely; and an association of the electric units with the magnetic ones is all that is necessary to account for radiation.”†

* Sir Oliver Lodge, *Journal of the Röntgen Society*, vol. 18, July, 1922.

† Sir Oliver Lodge, *Phil. Mag.*, vol. 41, p. 942, 1921.

CHAPTER XI

FOUR-DIMENSIONAL TUBES OR CALAMOIDS AS QUANTA

Absolute, true, and mathematical time, of itself, and from its own nature, flows equably without regard to anything external, and by another name is called duration.

Absolute space, in its own nature, without regard to anything external, remains always similar and immovable.

SIR ISAAC NEWTON

Henceforth space by itself and time by itself shall sink to mere shadows, and only a union of the two shall preserve reality.

MINKOWSKI

1. The Four-dimensional World of Minkowski

IN ordinary geometry the position of a point in space is fixed by means of three co-ordinates. But in relativity, time as well as position must be taken into consideration. An event, like the flashing of a lamp or the emission of an electron from an atom, which takes place at a certain point of space and at a certain instant of time may be called a "point-event." One measurement is required to determine the time of the event, and three measurements to determine the place. These are the four co-ordinates of the point-event. In other words, in the "space-time world" of Minkowski, four co-ordinates are required to fix a point-event. Thus the point-event is an element of the four-dimensional world as a point is an element of three-dimensional space.

The "interval" between two point-events involves both time and space, and when its measurement is defined in a certain way, all observers will agree as to the magnitude of an interval, or in mathematical language the expression for the interval is "covariant." In the world of Minkowski, as de Sitter has said, "a geometry of four dimensions is used, not a mere combination of a three-dimensional space and a one-dimensional time, but a continuum of truly fourfold order. This time-space is not Euclidean, since the time-component and the three space-components are not on the same footing, but its fundamental formula has a great resemblance to that of Euclidean geometry."

The four-dimensional world is usually regarded as a continuum of points. For a line to be continuous there must be no gaps or "holes" in it; the ideal line of the geometer is not a series of discrete black pencil marks on a sheet of paper, but is a one-dimensional continuum. The same idea may be extended to space of two or of three dimensions, and may be generalized so as to apply to any aggregate of elements numerically determined in such a way as to leave no holes. Such a set of elements of any kind forms a continuum. Now it is commonly assumed that the four-dimensional space-time world of Minkowski is a continuum, so that we may pass from one element to another—from one event to another—by traversing a path involving "successive" events. But it is just here that the quantum theory introduces a difficulty. According to Poincaré* the hypothesis of quanta is the only hypothesis leading to the law of Planck, and it involves the following proposition.

"A physical system is only susceptible of a finite number of distinct states; it jumps from one of these states to another without passing through a continuous series of intermediate states."

It may be added that Poincaré has shown that no small, or even finite, departures from the formula of Planck will enable us to escape from such discontinuities. The necessity for discontinuity is bound up with the fact that the total radiation at a given temperature is finite and not infinite.

2. Continuity and Discontinuity

The ultimate analysis of the notions of *continuity* and *discontinuity* will no doubt provide material for age-long discussion from the metaphysical side. We cannot, however, altogether escape the difficulties inherent in the quantum theory by shifting them on to the shoulders of the metaphysician. To a certain extent they have already burdened the physicist in connection with the atomic constitution of matter. Thus Larmor† writes: "The difficulty of imagining a definite uniform limit for divisibility of matter will always be a philosophical obstacle to an atomic theory, so long as atoms are regarded as discrete particles moving in an empty space. But as soon as we take the next step in physical development, that of ceasing to regard space as mere empty geometrical continuity, the atomic constitution of matter (each ultimate atom consisting of parts which are incap-

* Poincaré, *Dernières pensées* (Flammarion, Paris, 1913); Jeans, *Report on Radiation and the Quantum Theory*, pp. 35-6 (1914).

† Larmor, *Aether and Matter*, § 46, 1900.

able of separate existence, as Lucretius held) is raised to a natural and necessary consequence of the new standpoint. We may even reverse the argument, and derive from the ascertained atomic constitution of matter a philosophical necessity for the assumption of a *plenum*, in which the ultimate atoms exist as the nuclei which determine its strains and motions." To this passage Larmor appends a suggestive footnote. "It is perhaps not superfluous to point out the argument here involved against any tendency we might have to assign to the æther itself an atomic structure."

It is to be remembered that these passages were written before the development of the principles of relativity, and no doubt their author would at the present time express them differently.

A very interesting discussion of the question of continuity in relation to sub-atomic phenomena is to be found in Emile Borel's stimulating volume on *Space and Time*.* He propounds the question, whether, seeing that the motion of a solid body on which our geometry is based fails us completely on the sub-atomic scale, we should not try to construct an entirely different geometry of a discontinuous character. He suggests that this might be a way of attacking the difficulties raised by the theory of quanta.

"Following up a suggestion made by Riemann, to which, however, he did not seem to attach much importance, we might also ask whether the property which space seems to possess, of being in a sense the more certainly Euclidean the smaller the region is which we consider, does not disappear when we reach atomic or sub-atomic dimensions. Very small regions may have, as it were, a granular structure, and the Euclidean properties only hold good as averages."

One possible way of describing the discontinuity required by the quantum theory is to make the hypothesis that time itself is discontinuous, "Thus the universe would jump suddenly from one state to another, but in the interval between it would stand at rest. The different instants during which it stayed in the same state could not be distinguished from one another, so that we should be led to the discontinuous variation of time, to the atom of time" (Poincaré).

If, however, we adopt the view held by some supporters of the theory of relativity, that time ought not to be separated from space, we are led to the hypothesis that the space-time world is not a true continuum. With regard to such a suggestion Jeans † remarks: "The only type of atomicity which rela-

* Borel, *Space and Time* (Blackie, 1926).

† J. H. Jeans, *Atomicity and Quanta*, pp. 8, 55, 1926.

tivity can admit as being theoretically possible is one which finds its natural expression in terms of the four-dimensional continuum, the continuum in which the three dimensions of space and the one dimension of time enter as four equal partners. There can hardly be an atomicity of the continuum itself, for, if there were, a universal constant of the physical dimensions of space multiplied by time ought to pervade the whole of physical science. Nothing of the kind is even suspected, nor so far as I know, has ever been so much as surmised. Thus science can to-day proclaim with high confidence that both space and time are continuous."

Jeans suggests that the new atomicity may conceivably be an atomicity of the metric properties of the continuum, such as determine its curvatures.

It is clear from what has already been said that the view taken of the quantum must be profoundly affected by the principles of relativity. It will be well therefore to consider somewhat more carefully the nature and the consequences of these principles.

3. Relativity and the Space-Time World

In its simplest form the "restricted," or as it is sometimes called the "special," theory of relativity asserts that when we are dealing with uniform rectilinear motion, we can only speak of the mutual or relative motion of bodies. This statement is little more than an expression of the *kinematic* conception of motion, as signifying the alteration in the position of a body, and this can only be fixed by its distance from other bodies. But the statement may be extended so as to include the *physical* idea of motion, as a certain condition of the body which might conceivably be determined without reference to other bodies. We may then assert that it is impossible by means of observations made within a closed system (i.e. without reference to the surroundings) to ascertain whether or not the system is in uniform rectilinear motion.*

Einstein employed a second principle, deduced from the results of the Michelson-Morley experiment, which he called "the principle of the constancy of the velocity of light." This asserts that the velocity of light is an "invariant" of nature, always the same from whatever standpoint it is measured.

These two principles lead to a well-known set of equations (generally referred to as the "Lorentz transformation") by

* See Thirring, *The Ideas of Einstein's Theory*, pp. 2 and 166 (Methuen, 1921).

means of which measurements with reference to one particular frame of reference may be transformed so as to apply with respect to a second frame moving with velocity v with regard to the first.

The fundamental electrodynamic equations are usually based on the experimental conclusions of Coulomb, Ampère, and Faraday. The Maxwell field equations, which are used in describing a beam of light, will always be the same, even though a second frame of reference is employed moving with high velocity with respect to the first, provided the transformation is that given by Lorentz :

$$x' = \beta(x - vt), \quad y' = y, \quad z' = z, \quad t' = \beta(t - vx/c) \quad \text{II : I}$$

where $\beta = \sqrt{1 - v^2/c^2}$.

The equations are said to be *covariant* with respect to the transformation of co-ordinates.

Einstein, in his general theory of relativity, has taken a broader view, and stated as a fundamental principle: "The general laws of nature are expressed by mathematical equations which hold for all systems of co-ordinates, that is, they are covariant with respect to arbitrary substitutions."

Adopting this standpoint Leigh Page in *An Introduction to Electrodynamics*, instead of deducing the electrodynamic equations from the experimental results has pursued the opposite course and derived them from the principle of relativity.

Einstein introduced a general non-Euclidean four-dimensional time-space, and enunciated his law of motion by saying: "Particles which are not interfered with follow a geodesic line in the manifold." A geodesic in curved space or on a surface corresponds to a straight line in flat space. Larmor has laid stress on the application of the principle of least action in mechanical and electrodynamic problems. For example, an electron in moving through a magnetic field follows a geodesic line on a surface. It is this principle which led Einstein to his mode of stating the motion of bodies in space-time. The quantum theory may perhaps be thought of as providing the time-space world with certain partitions which impose restrictions on the motion of electrons or magnetons, which follow geodesic paths in accordance with the principle of minimum action. As Murnaghan* has expressed it: "Our guiding idea (the impossibility of action at a distance) will prompt us to say, following the example of Faraday in his electrical researches, that the geodesics of a gravitational space have a physical existence as distinct from a mere mathematical one."

The chief advantage of the variation principle of Hamilton (page 20) is its independence of the system of co-ordinates.

* Murnaghan in *Bird's Relativity and Gravitation*, p. 286 (Methuen).

"It must be pointed out that such things as length, velocity, energy, momentum, are not absolute, but relative, i.e. they are not attributes of the physical reality, but relations between this reality and the observer. Consequently the laws of conservation are not laws of the real world, like the law of gravitation, but of the observed phenomena. There is, however, one law which, already, before the days of relativity, had come to be considered as the most fundamental of all, viz. the principle of least action. Now action is absolute. Accordingly this principle retains its central position in Einstein's theory. It is even more fundamental than the law of gravitation, since both this law, and the law of motion, can be derived from it. The principle of least action, so far as we can see at present, appears to be *the* law of the real world." *

The connection between this principle and the quantum theory has been emphasized by Jean Becquerel,† who points out that the quantum is an element of action and consequently the theory of relativity demonstrates that Planck's constant is an invariant independent of the system of reference.

4. Tubes of Force in Four Dimensions

At the Edinburgh meeting of the British Association in 1921, Prof. E. T. Whittaker ‡ pointed out that the ordinary electrostatic and magnetic tubes in three dimensions were dependent on the relative state of rest or motion of the observer, and went on to discuss the properties of electromagnetic tubes of force in four dimensions. The author suggested the use of these tubes in quantum theory. Such a tube, or "calamoid," would involve both the electric and the magnetic vector and would satisfy all the requirements of the relativity theory. "Further, in the four-dimensional world it is action, not energy, which is conserved, so that the field appears open for a direct application of the quantum principle. The experimental physicist may feel somewhat appalled at the prospect of such a solution of his difficulties, but it may yet be necessary to invoke a four-dimensional tube of force as the unit brick from which a universe may be constructed." §

We proceed to consider further the details of this forecast.

Let x, y, z, t denote the co-ordinates of a point in the four-dimensional hyperspace. The word *surface* may be used to

* W. de Sitter in Bird's *Relativity and Gravitation*, p. 217 (Methuen).

† Jean Becquerel, *Le Principe de relativité et la théorie de la gravitation*,

p. 93.

‡ E. T. Whittaker, *Proc. Roy. Soc. Edin.*, vol. 42, p. 1, 1921.

§ H. S. Allen, *Nature*, vol. 108, p. 341, 1921.

mean a two-dimensional continuum in this hyperspace, so that a surface is defined by two equations between x , y , z and t .

The generalized tubes of force are surfaces defined in this way, and as it can be shown that they are independent of the arbitrary choice of a particular observer, they may be regarded as really objective. Whittaker first considers a region of free space with solitary electrons dispersed in it, and for simplicity assumes that the electric and magnetic vectors are everywhere at right angles to each other. He then shows that it is possible to derive a doubly infinite family of surfaces, which are covariant and are called the electropotential surfaces. These surfaces are represented by a pair of integral equations

$$\phi(x, y, z, t) = a, \quad \psi(x, y, z, t) = b \quad . \quad . \quad . \quad \text{II} : 2$$

where a and b are arbitrary parameters. It is because there are *two* arbitrary parameters in the equations of one of these surfaces that we speak of a doubly infinite family. These electropotential surfaces which exist in the four-dimensional world of space-time possess properties analogous to those of equipotential surfaces in electrostatics. In fact, when the field is static, each electropotential surface is wholly contained in three-dimensional space, and is an ordinary equipotential surface. By putting $t = t_0$ we may determine the intersection of an electropotential surface with the three-dimensional "space" as viewed by an observer at any instant t_0 . It then appears that "the intersections of the electropotential surfaces with the instantaneous space of an observer are the lines of magnetic force (in Faraday's sense) of that observer at that instant. In fact, each electropotential surface may be regarded as a single moving Faraday line of magnetic force. This applies to any observer since the electropotential surfaces are covariant: and therefore we see that the electropotential surfaces may be regarded as built up of the Faraday lines of magnetic force of the field, as perceived by different observers moving in all possible directions with all possible velocities."

In the same way another doubly infinite family of surfaces may be shown to exist in the electromagnetic field, which may be called magnetopotential surfaces. These surfaces reduce to the ordinary equipotential surfaces when the field is purely magnetostatic. In the general case, the intersections of the magnetopotential surfaces with the instantaneous space of an observer are the lines of electric force (in Faraday's sense) of that observer at that instant.

Thus in four-dimensional space the electropotential surfaces and the magnetopotential surfaces are two covariant families of surfaces, and it can be shown that they are everywhere absolutely orthogonal.

Whittaker then proceeds to show that a surface, Σ , can be found which is at every one of its points, half-orthogonal to the electropotential surface which passes through the point, and is also half-orthogonal to the magnetopotential surface which passes through the point. It may be remarked that the property here called "half-orthogonality" is really the same as what in ordinary three-dimensional geometry is simply called the "perpendicularity" of two planes.

When the field is purely electrostatic, or purely magnetostatic, the surfaces Σ become the ordinary Faraday tubes of force. In the general case the surfaces are a covariant family of surfaces, which may be called the tubes of force of the electromagnetic field or *calamoids* (from *κάλαμος*, a reed-pipe). Thus the Faraday electric and magnetic tubes are not distinct and rival things, but two limiting cases of the same thing.

It can be shown that these four-dimensional tubes of force possess important properties analogous to those belonging to ordinary Faraday tubes. In electrostatics there is a well-known result, which states that "the cross-section of a Faraday tube, multiplied by the value of the electric force, is constant along the whole length of the tube." The corresponding theorem in the four-dimensional world asserts that the cross-section of a thin calamoid (measured by the area which it cuts off on the electropotential surfaces which intersect it in curves) multiplied by the value of $\sqrt{(D^2 - H^2)}$ is constant along the whole length of the calamoid. Here D represents the electric vector, and H the magnetic vector at a point. The quantity

$$\sqrt{\{(\text{Electric Force})^2 - (\text{Magnetic Force})^2\}}$$

is well known to be covariant with respect to all Lorentz transformations. The calamoids are also covariant—which implies that they are the same, whatever be the observer whose measures of electric and magnetic force are used in constructing them.

It is not very easy to get a clear mental picture of the calamoids, especially in their most general form. Milner* has treated the question in a somewhat different way with the intention of extending Whittaker's results and enabling the reader to construct a representation of electromagnetic lines in hyperspace. In the electromagnetic field the directions of the electric and magnetic forces are in general neither along the same line nor at right angles to each other. Observers in different hyperplanes will form different conceptions of the strengths and directions of the electric and magnetic forces. Milner shows, however, that when viewed in a suitable hyperplane, i.e., when suitably transformed, the electric and magnetic forces at any

* S. R. Milner, *Phil. Mag.*, vol. 44, p. 705, 1922.

point of the general electromagnetic field can be made to *coincide in direction*. This direction determines an electromagnetic line, continuous through hyperspace. The procedure in constructing such a line, characterized by the collinearity along it of the transformed electric and magnetic forces, is precisely analogous to the method of constructing a line of force in an ordinary electrostatic field. From a set of electromagnetic lines an electromagnetic tube can be constructed. Four such tubes, mutually perpendicular, can be constructed containing any point, and each is characterized by the constancy of the flux of a specified quantity over its cross section. In a later paper Milner * shows that there is exact equivalence between the stress system of a four-dimensional electro-magnetic field and that of an electrostatic field in three dimensions.

5. Calamoids as Quanta

In the four-dimensional world action is of more importance than energy, and as the quantum theory points to an atomicity of action, it is of interest to see whether the representation of the field by means of four-dimensional tubes of force can be pressed into service to illustrate, or to elucidate, the character of the quantum.

Let dS represent an element of area of an electropotential surface at a point, and let dT represent an element of area of a magnetopotential surface at the same point. Then since dS and dT are "absolutely perpendicular" to each other, we see that $dSdT$ is an element of hypervolume, and is equal to $dx dy dz dt$. With the previous notation, in which D denotes the electric force and H the magnetic force,

$\sqrt{(D^2 - H^2)} \cdot dS$ = strength of the tube of force standing on dS ,
and

$\sqrt{(D^2 - H^2)} \cdot dT$ = strength of the tube of force standing on dT .

Therefore the products of the strengths of the two tubes

$$\begin{aligned} &= (D^2 - H^2) dS \cdot dT \\ &= (D^2 - H^2) dx dy dz dt \\ &= \text{an element of the action.} \end{aligned}$$

According to the accepted principles of the quantum theory, the integral of the action during any stationary state of the system is nh , where n is an integer, and h is Planck's constant. So we see that for a stationary state the products of the strengths of the two tubes, integrated over the region corresponding to the period, is an integral number of times Planck's constant.

* S. R. Milner, *Phil. Mag.*, vol. 46, p. 125, 1923.

It will be evident that we have done no more than touch upon the fringe of a region as yet unexplored. The experimental physicist finds a difficulty in working in this unfamiliar world, but it is clear that to the mathematician there is a wide field of investigation open in examining the properties of such discrete tubes of force in four dimensions. In particular it is desirable to study the character of the calamoids in the immediate neighbourhood of an electron or magneton. It will be necessary to take into account both "electricity" and "magnetism," but we may recall in this connection McLaren's conception of matter as a "hole in the æther," i.e. a region where the electromagnetic field equations cease to apply.

6. A Five-Dimensional Theory

In the general theory of relativity there is an apparent dualism of gravitation and electricity. It has been suggested that the inter-connection between the electromagnetic and the gravitational field may be considered from a single standpoint by employing a five-dimensional space. Kaluza * has given a theory in which the ten Einstein gravitational potentials and the four electromagnetic potentials are expressed in terms of the coefficients of the line element in a Riemannian space of five dimensions. The equations of motion of electrical particles in an electromagnetic field take the form of the equations of the geodesics. Klein † has developed this theory and shown that it may be put into relation with the undulatory form of the quantum theory given by de Broglie and Schrödinger (Chapter XVII). He further suggests that the origin of the quantum is to be found in the periodicity of the fifth dimension thus introduced, and that the atomicity of electricity may be interpreted as a quantum theory law.

Although such a mode of representation may be found convenient by the mathematician, it does not appear that it is able to throw much light on the physical aspect of the interpretation of the quantum.

* Kaluza, *Preuss. Akad. Wiss., Berlin, Ber.*, vol. 54, p. 966, 1921.

† Klein, *Zeits. f. Physik*, vol. 37, p. 895, 1926; *Nature*, vol. 118, p. 516, 1926.

CHAPTER XII

QUANTUM MAGNETIC TUBES IN ROTATION*

Since the density of matter is always positive, the electric charge-and-current inside an electron must be a space-like vector, the square of its length being negative. It would seem to follow that the electron cannot be built up of elementary electrostatic charges, but resolves itself into something more akin to magnetic charges.

A. S. EDDINGTON

1. The Electric Field of Magnetic Tubes in Rotation

THE atomicity required by the quantum theory must be intimately related to the existence of positive and negative electrons possessing distinctive properties, a fact which is not as yet satisfactorily explained. It has been shown earlier that the theory of quanta suggests the existence in three dimensions of discrete tubes of magnetic induction, corresponding to the "magnetic lines" which Faraday conceived of as physical entities, or in four dimensions of discrete electromagnetic tubes of force, the "calamoids" of E. T. Whittaker. In the present chapter our object is to discuss the properties of quantum magnetic tubes rotating about an axis, to determine their angular momentum and energy, to consider the electrostatic field set up by their rotation and to point out the possible connection between such a rotating tube and an electron. It may be said at the outset that this part of the work is frankly speculative in character.

Towards the end of 1920 Professor E. T. Whittaker drew the attention of the author to the nature of the electrostatic field which would be set up by magnetic tubes in rotation. If a set of magnetic tubes, resembling those due to a magnetic dipole, could be supposed to rotate like rigid wires about the axis of symmetry, an electric field would be produced which in the equatorial plane would vary inversely as the square of the distance from the centre of the system.

A large number of such systems oriented at random would produce, on the average, an electric field at a distance similar

* This chapter is based upon an article by the author in *Phil. Mag.*, vol. 49, p. 981, 1925.

to that due to an electrostatic charge, that is, a field varying inversely as the square of the distance. The equivalent electrostatic charge for a single system would be proportional to the magnetic moment (M) of the elementary magnet and to the angular velocity (ω) with which the system is rotating.

Further, Whittaker drew attention to the fact that for a given direction of the axis of the magnet there were *two* possible

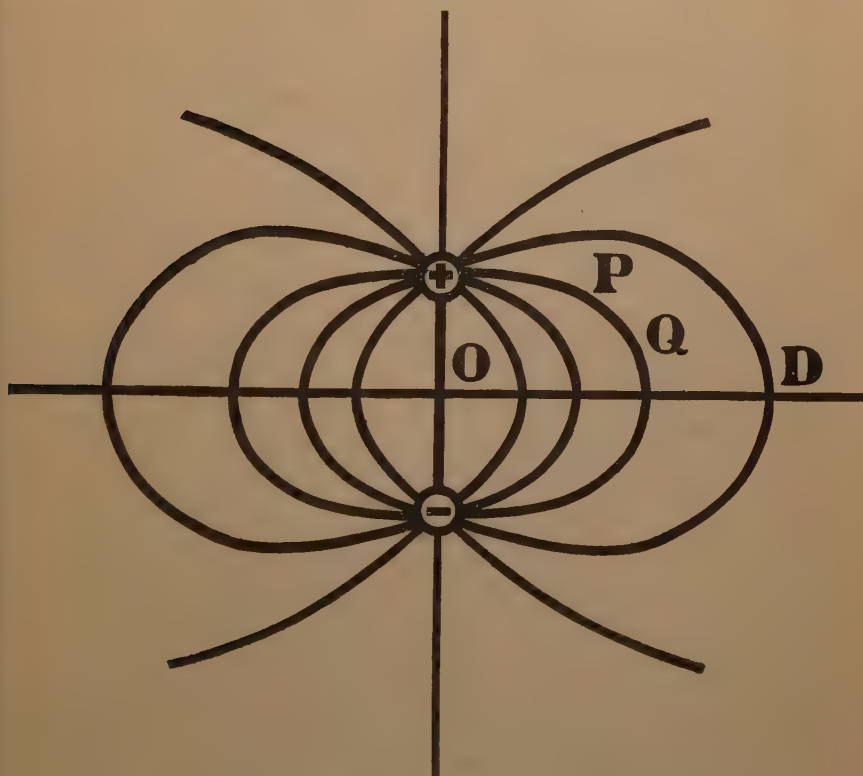


FIG. 23.—Magnetic Tubes due to a Dipole.

directions of rotation for the magnetic tubes, thus suggesting the possibility of interpreting the difference between positive and negative electric charges.

In imagination we may isolate a single quantum tube, such as that shown in Fig. 23, passing through the points P and Q , and discuss the electric field associated with that particular tube. It is to be noticed that the velocity at P will be less than that of light, even in the limiting case in which the velocity of the point D in the equatorial plane approaches that of light.

2. A Quantum Magnetic Tube in Rotation

We consider a single quantum tube such as would originate in a small magnet of magnetic moment M , and suppose it to be rotating with angular velocity ω about the axis of the magnet. Let A be the area of cross-section, ds the length of an element of the tube at any point P (Fig. 24).

The mass associated with each unit of volume of a magnetic

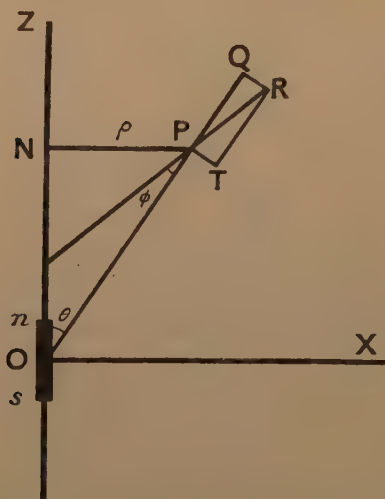


FIG. 24.—Field due to a Small Magnet.

field * is $KB^2/4\pi$, where $B = \mu H$, consequently the mass of an element of the tube at P is $\frac{KB^2}{4\pi} A ds$. Draw a perpendicular PN from P to the axis of the magnet, and let the length of PN be ρ . Then the angular momentum of this element about the axis is $\frac{KB^2}{4\pi} A ds \times \rho^2 \omega$. Now for a quantum tube the flux of magnetic induction, $BA = \mu HA = h/e$, and is constant along the tube. Therefore the angular momentum reduces to

$$\frac{K\mu}{4\pi} \cdot \frac{h}{e} \cdot \omega \cdot H \rho^2 ds.$$

The angular momentum for the whole tube is found by integrating this expression throughout the length of the tube.

* In this chapter the electric and magnetic co-efficients K and μ will be retained in the analysis.

The method of evaluating the integral is given in the paper cited where it is shown that

$$\int H \rho^2 ds = \frac{4M}{\mu} \quad . \quad . \quad . \quad 12:1$$

Substituting this value in our expression for the angular momentum we find that the total angular momentum for the single quantum tube is

$$\frac{K\mu}{4\pi} \cdot \frac{h}{e} \cdot \omega \cdot \frac{4M}{\mu} = \frac{KM}{\pi} \cdot \frac{h}{e} \cdot \omega \quad . \quad . \quad . \quad 12:2$$

And so we see that the magnetic tube which we are considering has an equivalent moment of inertia

$$I = \frac{KMh}{\pi e}.$$

Remembering that the angular velocity, ω , can be expressed in terms of the frequency by writing $\omega = 2\pi\nu$, we find that the

$$\text{Angular Momentum} = \frac{2KMh}{e} \nu \quad . \quad . \quad . \quad 12:3$$

We can now write down the kinetic energy of the quantum tube, for it is found by multiplying the angular momentum by $\frac{1}{2}\omega$, and the Kinetic Energy = $\frac{1}{2} \frac{K\omega h}{\pi e} \omega^2$ or $\frac{1}{2} I \omega^2$

$$= \frac{2\pi KMh}{e} \nu^2 \quad . \quad . \quad . \quad 12:4$$

3. The Equivalent Charge of a Rotating Tube

When a magnetic tube is in motion, it produces an electric field. In the case of the rotating quantum tube already considered the electric field set up at a point D in the equatorial plane is equal to Bv where v is the velocity of the rotating tube at that point. If the distance OD is a , the velocity $v = a\omega$, and the electric field is $Ba\omega$, or $2\pi aB\nu$.

Let us assume that the electric field at D is the same as would be produced by an electrostatic charge E at the point O, and then determine the value of that charge. As the two fields are assumed to be equal,

$$\frac{E}{Ka^2} = Bv = Ba\omega = 2\pi aB\nu \quad . \quad . \quad . \quad 12:5$$

Now the magnetic field at D is supposed to be due to an

dimensions. This means that the velocity of the point D (Fig. 23) approaches the velocity of light, so that $v = a\omega = c$. Consequently, ω being $2\pi\nu$, $2\pi\nu a = c$ and thus

$$a = \frac{c}{2\pi\nu} = \frac{c}{\frac{4\pi\nu_{\infty}}{a^2}} = \frac{a^2 c}{4\pi\nu_{\infty}} = 3.86 \times 10^{-11} \text{ cm.} \quad 12:14$$

A more convenient expression for the radius is obtained in terms of the innermost orbit in Bohr's theory of the hydrogen atom. This may be written

$$a_1 = \frac{ac}{4\pi\nu_{\infty}}$$

Therefore $a = aa_1$ 12:15

Assuming $e = 4.774 \times 10^{-10}$ E.S.U., the numerical value for a is $1/137$. The radius of the electron is $1/137$ times the radius of this innermost orbit.

From the relation $E = KM\omega$ the magnetic moment of the elementary magnet is found to be

$$M = \frac{\mu h e}{2\pi m} \quad . \quad . \quad . \quad . \quad . \quad 12:16$$

This is twice the magnetic moment of the Bohr magneton, and it may be mentioned that it corresponds very closely with the value derived from the saturation intensity of magnetization of iron, which according to Ewing * is nearly 2×10^{-20} c.g.s. units per atom of iron.

The ratio of the angular momentum to the magnetic moment for the electron here considered has the value $2m/\mu e$, which is equal to the gyromagnetic ratio deduced from the theory of electron orbits by O. W. Richardson.†

Case II.— In the preceding calculations we have neglected the energy associated with the frequency characteristic of the tube itself, energy which may correspond, possibly, to an internal vorticity. When this is taken into account we have to deal with an amount of energy $h\nu_r$, due to the rotation of the whole tube about an axis with frequency ν_r , and also an amount of energy $\frac{1}{2}h\nu_s$, which is due to the internal condition of the tube, and would be present in the tube when not rotating, ν_s being the frequency appropriate to the stationary tube. These quantities are additive, and as there are two possible directions of rotation we have for the energy in one case $h\nu_r + \frac{1}{2}h\nu_s$, and in the other $h\nu_r - \frac{1}{2}h\nu_s$.

As the first amount is clearly greater than the second let us

* J. A. Ewing, *Proc. Roy. Soc. Edin.*, vol. 42, p. 124, 1922.

† O. W. Richardson, *Phys. Rev.*, vol. 26, p. 248, 1908; *Proc. Roy. Soc.*, vol. 102, p. 538, 1923.

identify the first case with a positive electron, the second with a negative electron.

Let m_p be the mass of the proton (+ve electron), and m_c the mass of the corpuscle (—ve electron). Then, in accordance with the principle of relativity,

$$\begin{aligned} m_p c^2 &= h\nu_r + \frac{1}{2}h\nu_s \\ m_c c^2 &= h\nu_r - \frac{1}{2}h\nu_s \end{aligned} \quad . \quad . \quad . \quad . \quad 12:17$$

That is to say, we have here expressions for the mass of the proton and the corpuscle expressed in terms of these two frequencies ν_r and ν_s . Dividing the first by the second we get at once

$$\frac{m_p}{m_c} = \frac{2\nu_r + \nu_s}{2\nu_r - \nu_s},$$

and therefore

$$\frac{m_p + m_c}{m_p - m_c} = \frac{2\nu_r}{\nu_s} \quad . \quad . \quad . \quad . \quad 12:18$$

The value found experimentally for $\frac{m_p}{m_c}$ is very nearly 1833 (Bucherer and Ladenburg). Using this numerical value we find $\frac{\nu_r}{\nu_s} = 0.50051$. This means that the frequency of rotation of our magnetic tube is rather larger than one half the frequency characteristic of the stationary tube.

It is convenient to express the frequency in terms of the fundamental Rydberg frequency $\nu_\infty = \frac{2\pi^2 m e^4}{h^3 K^2}$. Putting $\frac{2\pi e^2}{hcK} = \alpha$ this relation may be written

$$mc^2 = \frac{2h\nu_\infty}{\alpha^2}.$$

From the equations we find without difficulty the results

$$\left. \begin{aligned} \nu_r &= \frac{\nu_\infty \left(\frac{m_p}{m_c} + 1 \right)}{\alpha^2} \\ \nu_s &= \frac{2\nu_\infty \left(\frac{m_p}{m_c} - 1 \right)}{\alpha^2} \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad 12:19$$

Substituting the numerical values

$$\nu_\infty = 3.271 \times 10^{15}, \quad \frac{1}{\alpha} = 137,$$

we find

$$\left. \begin{aligned} \nu_r &= 1.126 \times 10^{23} \text{ sec}^{-1} \\ \nu_s &= 2.250 \times 10^{23} \text{ sec}^{-1} \end{aligned} \right\}$$

If we assume, as in Case I, that $\alpha\omega_r = c$, we find as a limiting value for α , the radius of the electron, 4.24×10^{-14} cm. It

should be noticed that on these assumptions the size of a negative electron does not differ from the size of a positive electron, the radius being a quantity of the same order of magnitude as the estimate of the radius of an atomic nucleus obtained by Rutherford from experiments on the scattering of α particles. The radius of the negative electron on the classical theory is well known to be a quantity larger than this, but that estimate is derived from the assumption that the electron may be treated as a charged sphere.

Although no quantitative explanation has yet been found for the frequencies ν_r and ν_n , which have been assigned so as to give the masses actually observed, it may be suggested that they are in some way determined by the limiting condition that the velocity of the extreme edge of the rotating tube cannot exceed the velocity of light.

It is interesting to compare with the suggestions here made a surmise as to the relation between positive and negative electricity put forward independently by Sir Oliver Lodge in his Presidential Address to the Röntgen Society on November 6, 1923.

"Let us suppose then that round the nucleus of an atom the æther is in a state of violent rotation. It might even be suggested that a proton itself is always and constitutionally in a state of circulation at a speed comparable to the velocity of light, and that in this way its mass is accounted for, as distinguished from the much smaller mass of the electron, which presumably is not in a state of rotation. We might go so far as to surmise—as indeed we do for many other reasons, connected with the transmission of waves by a vortex filled medium—that the normal æther contains a constitutional rotation comparable to the velocity of light, and that upon this, when a pair of electric units are being somehow generated, two equal opposite rotations are superposed; one in opposition to the original rotation, giving a net result zero; the other in the same direction, giving a result slightly nearer to the velocity of light than before, conceivably sufficient to cause what would otherwise be the mirror-image of the negative electron to have a mass 1,850 times as big."

5. Discussion of the Electronic Models

The fundamental electric charge here postulated possesses axial and not spherical symmetry. Further, it exhibits magnetic as well as electric properties. It is indeed a "magneton" which serves also as an "electron." The spinning electron (Chapter XVI) employed by Goudsmit and Uhlenbeck may be regarded

as complementary to the system under discussion. Either of these models would satisfy the requirements of experimental work, such as that of Stern and Gerlach, necessitating both magnetic and electric characteristics in the fundamental physical entities.

According to the hypothesis advanced *each quantum tube may be regarded as a potential electron*. In Chapter X it was suggested that the emission of radiation consisted in, or was consequent upon, the liberation of a quantum tube from an atomic or molecular system. Taking this suggestion in connection with the present hypothesis some light is thrown on the remarkable reciprocal relation between radiation and electrons. With characteristic boldness Sir Oliver Lodge * has discussed this problem in an address on *Æther and Electrons* and suggested that the actual generation of an electron by means of light is not an altogether impossible idea.

We may anticipate one result from a later chapter and mention that de Broglie has postulated an "internal process" of a definite frequency in connection with *any* moving particle. On the theories advanced by de Broglie, Einstein, and Schrödinger, electrons, both positive and negative, and light quanta all alike involve periodic phenomena. Such a conception is in harmony with the present conception of magnetic tubes possessing an internal spin of assigned frequency. Again, J. D. van der Waals † has suggested that this view of the periodic character of atomic structure can be expressed so as to involve spatial limitations of the atoms, just as we have found limits to the size of the positive or negative electron.

The picture of an atomic nucleus suggested by the foregoing considerations is that of a set of magnetic tubes rotating about a common axis with the same angular velocity, some of the tubes representing positive, the remainder, and smaller number negative electrons.

Outside the nucleus we should expect to have in addition a set, or sets, of outer magnetic tubes, of larger size, rotating or capable of rotating about the same axis so as to give rise to the external magnetic and electric field due to the atom. These tubes may be supposed to rotate with very much smaller angular velocity than the inner set. For instance, they might have an angular velocity comparable with that of the radius vector to an electron in one of the Bohr orbits. In that case the mass to be associated with these outer tubes would be very small in comparison with the mass of the nucleus.

Finally these results and suggestions may be considered in

* Sir Oliver Lodge, *Nature*, vol. 112, p. 185, August 4, 1923.

† van der Waals, K. Akad. Amsterdam, *Proc.*, vol. 29, p. 899, 1926.

relation to the quantum mechanism in the atom described by Whittaker. For the magnetic wheel in rotation, which he uses as an illustrative model, is equivalent to a set of rotating magnetic tubes, and the structure is essentially a mechanism by which an electrostatic field is produced by the motion of these tubes. Stress may be laid on Whittaker's argument that when a charged particle is approaching an atom, the electric field about the atom is not permanent, but is evoked by the approach of the particle. The approaching charge induces within the atom a "magnetic current," i.e. the magnetic analogue of an electric current.

Also it is worthy of special note that in this mechanism the electric separation in the atom, which is caused by the collision with the bombarding particle (carrying an electron charge), is precisely a separation of two electronic charges $+e$ and $-e$. The process might be described as the manufacture of a positive and negative electron, or at least as a stage in such manufacture. Again, the emission of radiation by the mechanism may be regarded as the liberation of a magnetic tube from the structure.

Although the models we have described are admittedly speculative, they do possess the advantage of emphasizing the magnetic nature and the periodic character of all fundamental physical processes and systems. "Until fuller certainty comes, it is well that every hypothetically possible line of advance should be explored."* The suggestions of this chapter are put forward in the conviction that these words are in a special sense true at the present stage in the development of physical theory.

* W. Peddie, *Proc. Roy. Soc. Edin.*, vol. 42, p. 223, 1922.

PART III

DEVELOPMENT OF THE QUANTUM THEORY

CHAPTER XIII

PLANCK'S CONSTANT AND THE ELECTRON

That there are discrete mechanical and electrical systems, characterized by quantum conditions and marked out from the infinite continuity of "classically" possible states, appears certain. But where does the deeper cause lie, which brings about this discontinuity in nature? Will a knowledge of the nature of electricity and of the constitution of the electromagnetic field serve to read the riddle?

FRITZ REICHE, *The Quantum Theory*, 1922

1. The Quantum and the Electron

IN the last chapter of his book, *The A B C of Atoms*, Bertrand Russell refers to some of the problems connected with the new physics and relativity. When we wish to consider what is happening in some very small region, we must not take merely a small region of space, but a small region of space-time. "This leads us to consider, not merely the energy at an instant, but the effect of energy operating for a very short time; and this, as we saw, is of the nature of action. . . . It is a fact which must be significant that action thus turns out to be fundamental both in relativity theory and in the theory of quanta. But as yet it is impossible to say what is the interpretation to be put upon this fact; we shall probably have to wait for some new and more fundamental way of stating the quantum theory."

In atomic physics we find a number of questions which have hitherto seemed unanswerable. "We do not know why there are two kinds of electricity, or why opposite kinds attract each other while similar kinds repel each other. This dualism is one of the things which is intellectually unsatisfying about the present

condition of physics. . . . We find it hard to rest content with the existence of unrelated absolute constants, such as Planck's constant and the size of an electron, which, so far as we can see, might just as easily have had any different magnitude. To the scientific mind such facts are a challenge, leading to a search for some way of inter-relating them and making them seem less accidental."

The possibility of establishing a relationship between Planck's constant, h , and the electron charge, e , was suggested in 1911 by Einstein, who pointed out that the product hc (where c is the velocity of light) has the same physical dimensions as the square of an electric charge, when the charge is measured in electrostatic units. Jeans commented on this at the Birmingham meeting of the British Association in 1913, and in the first edition of his *Physical Society Report on Radiation and the Quantum Theory* (1914) wrote: "In point of fact, $hc/2\pi$, if not exactly equal, is almost equal to $(4\pi e)^2$, i.e. to the square of the strength of a tube of force binding two electrons. This suggests that the atomicity of h may be associated with the atomicity of e ."

Various attempts have been made to establish a relation between hc and e^2 , and the more important of these will be discussed in the present chapter, although it may be said at the outset that no final and entirely satisfactory solution has yet been reached. The problem may be attacked in two ways, either by endeavouring to find an exact numerical relation between the quantities involved, or by finding some hypothesis of a physical nature which may serve to link together the two types of atomicity.

Jeans * has given an illuminating account of the nature of the atomicity demanded by the theory of electrons and by the quantum theory.

"Electric charges are a consequence of, or at least are associated with, a curving or crumpling of space, but so far as pure geometry goes there is no restriction on the extent of this crumpling, so that our geometer, reasoning from geometry alone, might expect to find charges of all possible amounts, whereas in actual fact electric charges occur only in multiples of a definite unit, the charge of an electron. It is clear, then, that there is something more than geometry underlying the phenomena of Nature; the whole phenomenal universe may be geometry with restrictions if we like, but not merely the geometry which is obtained by generalizing the geometry of Euclid until we can generalize no further. Space can be crumpled up

* J. H. Jeans, *Nature*, vol. 115, p. 364, 1925.

qualitatively in all the ways known to geometry but not quantitatively; the uniformity of the electronic charge must in some way represent an absolute restriction on the measure of the crumpling.

"Each particle of matter—each electron let us say—occupies one point of space at any one instant of time, and the succession of these points will form a line in the four-dimensional space-time continuum—the 'world-line' of the electron. In the neighbourhood of this world-line there is a deformation of the continuum due to the existence of the electron.

"The near approach of two electrons or of any two charged particles is represented by a near approach of their world-lines in the four-dimensional continuum. Each world-line is surrounded by its associated deformation, and in regions in which the world-lines are near to one another the adjacent regions of the continuum will be doubly deformed.

"A priori there are two possibilities open. The first is that the two deformations are merely additive, just as, when two ships approach, each making its own wash (or deformation of the surface of the sea), the height of wash at any point is the sum of the heights of the washes made by the two ships independently. The second possibility is that, as there have been found to be restrictions on the amount of deformation associated with the two separate world-lines, there may be a further restriction on the deformation arising from their combination.

"In actual fact the former alternative appears to prevail when one or both of the charged particles are 'free' electrons, but the latter alternative when they are 'bound' together; that is, when they are permanently describing orbits about one another. It is these latter restrictions that have given rise to the theory of quanta. Just as the restrictions associated with single world-lines give rise to an atomic constant e , the charge on an electron, so the restrictions associated with pairs of world-lines give rise to a second atomic constant. This is generally taken to be h , Planck's constant, but in many respects it is more appropriate to regard the product hc as the second constant, where c is the velocity of light. It is significant that hc is of the same physical dimensions as e^2 and so may be regarded as being the same thing as e^2 except for a numerical multiplier. Thus while the restrictions connected with one world-line introduce e , those connected with two world-lines, depending only on e^2 , introduce no essentially new constant, whence it may reasonably be suspected that the two sets of restrictions are merely different aspects of one and the same set. It looks as though the atomicity of the quantum theory is only another aspect of the atomicity of electric charges."

2. The Relation of Lewis and Adams and the Values of the Quantum Constants

A quantitative relation between h , c , and e was proposed by Lewis and Adams,* who derived it by employing their "theory of ultimate rational units." They believe that ultimately "all universal constants will prove to be pure numbers, involving only integral numbers and π ." This assumption has been criticized by Bridgman and N. R. Campbell,† and even apart from other objections, may well prove too sweeping. For instance, in an attempt to obtain a relation between h and e , the author was led to consider the series

$$S_3 = 1 + \frac{1}{2^3} + \frac{1}{3^3} + \dots \quad \text{I3:1}$$

which has not, as yet, been expressed in terms of integral numbers and π .

Lewis and Adams obtain their relation by assuming that the constant a of Stefan's radiation law $E = aVT^4$, can be expressed in the form

$$a = k^4/(4\pi e)^6 \quad \text{I3:2}$$

where k is Boltzmann's constant. To obtain h , it is necessary to assume the truth of Planck's formula, by integrating which we obtain

$$a = \frac{8\pi^5 k^4}{15h^3 c^3} \quad \text{I3:3}$$

and on identifying the two values of a , we find

$$15h^3 c^3 = 8\pi^5 (4\pi e)^6,$$

or

$$hc = \sqrt[3]{\left(\frac{8\pi^5}{15}\right)} \times (4\pi e)^2 \quad \text{I3:4}$$

We may note that the numerical factor $8\pi^5/15$ which occurs under the cube root may be written as $48\pi S_4$, where

$$S_4 = 1 + \frac{1}{2^4} + \frac{1}{3^4} + \dots = 1.0823 \quad \text{I3:5}$$

It is convenient to write the relation of Lewis and Adams in the form

$$\frac{2\pi e^2}{hc} = q \quad \text{I3:6}$$

where

$$q = \frac{(15/\pi^2)^{1/3}}{4\pi^2} = (7.28077 \dots) \times 10^{-3} \quad \text{I3:7}$$

* Lewis and Adams, *Phys. Rev.*, vol. 3, p. 92, 1914. Lewis, *Phil. Mag.*, vol. 45, p. 266, 1923; vol. 49, p. 739, 1925.

† N. R. Campbell, *Phil. Mag.*, vol. 47, p. 159, 1924.

In a paper communicated to the Physical Society of London in February, 1915, the author * drew attention to the importance of this constant, and pointed out some curious numerical relations between electronic and atomic constants, in which it occurs. Even if the numerical factor suggested by Lewis and Adams should require modification in the light of a complete theory revealing the connection between the quantum and the electron,

we may still regard $\frac{2\pi e^2}{hc}$ as a fundamental physical constant—a

pure number which cannot differ greatly from the value given above. Such a constant has, in fact, been employed by Sommerfeld † (see p. 179) in his important work on the fine structure of spectrum lines, where it is denoted by α , and called “the fine structure constant.” We shall use this notation and write

$$\frac{2\pi e^2}{hc} = \alpha \quad . \quad . \quad . \quad . \quad . \quad 13 : 8$$

If the suggestion of Lewis and Adams is correct, $\alpha = q$. This, however, is open to doubt, because of the complicated form of the expression for q , in spite of the fact that recent experimental determinations of the quantum constant, h , point to α being very nearly equal to q . Even if the theory of ultimate rational units were to be accepted, it might be argued that it is not in the expression of Stefan's law that we should expect simplicity, but rather in the expression for α , which depends upon the relation between the quantum constant and the fundamental unit of electric charge.

In an able paper on atomic constants and dimensional invariants, A. C. Lunn ‡ has discussed various expressions for the constant α , which he denotes by S . “The kernel of the problem seems likely to be the determination of the invariant S , which is already fundamental in Sommerfeld's theory and will doubtless prove to be of much wider importance. A theoretical explanation of its meaning and value will probably mark the achievement of a satisfactory logical connection between the electron theory and the quantum theories.” Lunn points out that any number of expressions may be found, containing only integers and π , any one of which will give fair numerical coincidence with the experimental value of S or α . To the list which he gives may be added $1/\alpha = 8\pi^2\sqrt{3} = 136.8$ or $\alpha = .007312$. “One can hardly have much hope of obtaining

* H. S. Allen, *Proc. Phys. Soc.*, vol. 27, p. 425, 1915. See also *Nature*, vol. 112, p. 622, 1923.

† Sommerfeld, *Annalen d. Physik*, vol. 51, pp. 1–94, 125–67, 1916.

‡ A. C. Lunn, *Physical Review*, vol. 20, p. 1, 1922.

a true theoretical value of such a constant by pure conjecture based on numerical coincidence merely."

VALUES OF QUANTUM CONSTANTS

$$e = 4.774 \times 10^{-10} \text{ E.S.U.}$$

$$c = 2.9986 \times 10^{10} \text{ cm. sec.}^{-1}.$$

	h	a	a^2	$1/a$	$1/2\pi a$
Ladenburg 1920	6.540×10^{-27}	7.299×10^{-8}	5.332×10^{-5}	137.0	21.80
Sommerfeld 1924	6.545	7.295	5.322	137.1	21.82
Planck . . 1900	6.550	7.291	5.316	137.2	21.83
Birge . . 1919	6.5543	7.286	5.309	137.2 ₅	21.84
Birge . . 1923	6.557	7.283	5.304	137.3	21.85
Duane* . . 1921	6.558	7.282	5.303	137.3	21.85 ₅
Lewis and Adams	6.5592	7.28077	5.30096	137.35	21.860

In the table are shown the values of a and of related constants corresponding to several values of h , assuming Millikan's value for the electron charge, $e = (4.774 \pm 0.004) \times 10^{-10}$ E.S.U., and the velocity of light as $c = 2.9986 \times 10^{10}$ cm. sec.⁻¹, as given by Kaye and Laby.† This value of c is in close agreement with a recent determination of the velocity of light by Michelson,‡ who found $c = 2.99796 \times 10^{10}$. R. Ladenburg§ has published a critical discussion of the various determinations of Planck's constant made up to 1920, giving $h = 6.54 \times 10^{-27}$ erg sec. as the surest value, and R. T. Birge has computed the most probable value of the constant derived from seven distinct methods, his final mean value (in July, 1919) being

$$h = (6.5543 \pm 0.0025) 10^{-27} \text{ erg sec.}$$

Birge || employs the relation of Lewis and Adams as the basis of one of his methods, a procedure which is not in harmony with our present purpose, as we are now concerned with the agreement between values derived from such mathematical expressions, and those found by direct experiment. It is clear from the table that as the value $h = 6.5592 \times 10^{-27}$ calculated from the formula of Lewis and Adams, which may be written

* The value found by Duane, Palmer and Yeh in 1921 has been corrected by using Wagner's value of the lattice constant (Ladenburg, *Handbuch der Physik*, vol. 23, p. 299).

† Kaye and Laby, *Physical and Chemical Constants*, 1921.

‡ Michelson, *Studies in Optics*, p. 137, 1927.

§ R. Ladenburg, *Jahrbuch der Radioaktivität und Elektronik*, vol. 17, p. 93, 1920; Planck's *Elementares Wirkungsquantum und die Methoden zu seiner Messung*, S. Hirzel, 1921.

|| R. T. Birge, *Phys. Rev.*, vol. 14, p. 361, 1919; *Nature*, vol. 111, p. 287, 1923.

$$h = \frac{16\pi^2 e^2}{c} \sqrt[3]{\frac{8\pi^5}{15}} \quad . \quad . \quad . \quad 13:9$$

is the largest recorded, the omission of this method would tend to diminish the slightly lower values found by Birge. In a note published in 1923 Birge, using the value

$$e/m = (1.761 \pm 0.002) \times 10^7$$

found by H. D. Babcock of Mount Wilson Observatory from the Zeeman effect, deduced from Bohr's theory of the Rydberg constant (assuming $N_\infty = 109737$)

$$h = (6.556 \pm 0.011) \times 10^{-27} \text{ erg sec.}$$

This is in close agreement with his previous most probable value, and coincides almost exactly with Duane's value from the continuous X-ray spectrum. The final most probable value is given as 6.557×10^{-27} erg sec. Birge believes that the error in this quantity can be scarcely more than a few units in the last place, unless Millikan's value of e is unexpectedly in error.

The table also includes the value of h calculated by Sommerfeld,* following L. Flamm, by employing semi-spectroscopic units, viz.:

$$h = (6.545 \pm 0.009) 10^{-27}$$

Sommerfeld suggests that this is (in 1924) the truest value of the quantum of action. It is of interest to observe that Planck's original estimate of the quantum constant, 6.55×10^{-27} , occupies a mean position in the list of experimental determinations.

In a discussion of later date (1926) Birge † gives the value

$$h = (6.559 \pm 0.0044) \times 10^{-27}$$

deduced from the work of E. O. Lawrence on the ionization potential of mercury. This is in very good agreement with the result obtained by Duane, Palmer and Yeh when corrected for the grating constant of calcite, and it is noteworthy that it is extremely close to the value obtained from the relation of Lewis and Adams.

In considering the most probable value of the basic constants of physics due weight must be given to the known relations between these quantities. The question has been discussed by Birge (*loc. cit.*), who points out that one can sometimes measure a certain function of two or more quantities with a greater precision than that attainable in the measurement of each

* Sommerfeld, *Atombau und Spektrallinien* (4th German edition, 1924), p. 476.

† Birge, *Science*, vol. 64, p. 180, 1926.

separate quantity. He has obtained the following *system* of values for certain fundamental constants:—

$$\begin{aligned}e &= 4.7755 \times 10^{-10} \text{ E.S.U.} \\c &= 2.9986 \times 10^{10} \text{ cm. sec.}^{-1}. \\h &= 6.560 \times 10^{-27} \text{ erg sec.} \\e/m &= 1.760 \times 10^7 \text{ E.M.U.}\end{aligned}$$

This system not only satisfies the known relations between these quantities, but agrees within limits of error with the most probable value of *each* constant, as determined by methods independent of any such relations.

Employing these data we find $\alpha = 0.0072844$ and $1/\alpha = 137.28$.

3. Relations involving the Constant α

It is clear that any relation between physical quantities involving Planck's constant, h , may be expressed in terms of α . In several cases the relation assumes a very simple form when so expressed, and it may be useful to notice certain instances—some of which have been mentioned previously—as they may prove suggestive in seeking for a physical interpretation of the constant.

A. Bohr's Theory of the Hydrogen Atom.

When an electron is describing a circular orbit about a massive nucleus (charge E), the *velocity* in the orbit is given, as we have seen in Chapter IV, by

$$v_n = \frac{2\pi Ee}{nh} \quad . \quad . \quad . \quad . \quad . \quad 13:10$$

where n is the quantum number for the orbit in question.

Putting $E = Ze$, where Z is the atomic number, we find

$$\frac{v_n}{c} = \frac{Z}{n}\alpha \quad . \quad . \quad . \quad . \quad . \quad 13:11$$

Hence for the innermost orbit of the hydrogen atom

$$\frac{v_1}{c} = \alpha \quad . \quad . \quad . \quad . \quad . \quad 13:12$$

Thus the constant α appears as the ratio of the velocity in this the most stable orbit, to the velocity of light.

It has been pointed out by Siracusano* that the formula for the velocity of an electron in the innermost orbit described about a nucleus of atomic number Z , may be regarded as imposing a limit on the value of Z . In the limiting case when $v = c$, we should have $Z = 1/\alpha$, showing that Z cannot exceed 137.

* Siracusano, *Accad. Lincei, Atti*, vol. 5, p. 114, 1927.

Expressed as a frequency Rydberg's constant for a massive nucleus may be written

$$\frac{2\pi^2 me^4}{h^3} Z^2 = \nu_{\infty} Z^2,$$

using ν_{∞} as an abbreviation for $\frac{2\pi^2 me^4}{h^3}$. We may now write down expressions of a convenient form for the radius of the orbit, and other atomic quantities.

The *radius* of the n th orbit, a_n , is

$$a_n = \frac{n^2}{4\pi Z} \frac{ac}{\nu_{\infty}} \quad . \quad . \quad . \quad . \quad \text{I3 : I3}$$

The *frequency* of revolution of the electron in the orbit may be written

$$\nu_n = \frac{2Z^2}{n^3} \times \nu_{\infty} \quad . \quad . \quad . \quad . \quad \text{I3 : I4}$$

The *kinetic energy* T , which is numerically the same as Bohr's W , may be expressed as

$$T = \frac{1}{2} n h \nu_n \quad . \quad . \quad . \quad . \quad \text{I3 : I5}$$

This in fact was the form adopted by Bohr as the most suitable expression for the kinetic energy, and may be regarded as the condition determining stationary orbits.

The *electrostatic energy*, numerically equal to $\frac{Ee}{a}$, can be expressed in the form

$$m \frac{Z^2}{n^2} \alpha^2 c^2 \quad . \quad . \quad . \quad . \quad \text{I3 : I6}$$

It may, accordingly, be interpreted as kinetic energy, and be expressed as $n h \nu$.

A result of interest is obtained by combining the two relations :

$$\frac{2\pi e^2}{hc} = \alpha \text{ and } \nu_{\infty} = \frac{2\pi^2 me^4}{h^3}.$$

On eliminating e we find

$$mc^2 = \frac{2h\nu_{\infty}}{\alpha^2} \quad . \quad . \quad . \quad . \quad \text{I3 : I7}$$

Now, according to Einstein's theory of relativity, mc^2 represents the energy of the electron as judged from a co-ordinate system moving with it. So we see that this energy may be represented as an energy quantum having frequency $2\nu_{\infty}/\alpha^2$, or if we prefer it, as two energy quanta of frequency ν_{∞}/α^2 .

B. Sommerfeld's Theory of Fine Structure.

Sommerfeld seeks for the explanation of the fine structure of the hydrogen and similar series lines in the relativistic treatment

of the motion of the electron round the nucleus. Assuming the mass of the electron to be a function of its velocity, the equation of the orbit is found in the form

$$\frac{1}{r} = C(1 + \varepsilon \cos \gamma \phi) \quad . \quad . \quad . \quad . \quad 13:18$$

where $\gamma^2 = 1 - \left(\frac{e^2}{p_0 c}\right)^2$, and p is the constant value of the angular momentum, which in accordance with quantum principles is equal to $nh/2\pi$. Sommerfeld now introduces a critical or "universal" moment of momentum, designated by p_0 , where $p_0 = e^2/c$. Thus the ratio of the critical moment of momentum to the quantized moment, p , is

$$\frac{p_0}{p} = \frac{2\pi e^2}{hc} = \alpha \quad . \quad . \quad . \quad . \quad 13:19$$

for hydrogen in the one quantum state.

We may now write

$$\begin{aligned} \gamma^2 &= 1 - (p_0/p)^2 \\ &= 1 - (\alpha/n)^2 \quad . \quad . \quad . \quad . \quad 13:20 \end{aligned}$$

and if γ differs but slightly from unity the orbit may be regarded as an ellipse with slowly moving perihelion.

It is then shown that the fine-structure constant, appearing in the separation in wave-numbers of the hydrogen doublet, is

$$\Delta\nu_H = \nu_\infty \alpha^2/2^4 \quad . \quad . \quad . \quad . \quad 13:21$$

where ν_∞ is Rydberg's constant.

C. The Stark Effect.

By the action of external forces such as those arising from an electric or magnetic field much greater changes can be produced in spectral lines than those just considered. In 1913 Lo Surdo* and J. Stark† independently discovered the effect of an electric field in splitting the Balmer lines of hydrogen into a number of components. The observations received a theoretical explanation on the basis of the quantum theory through the work of Schwarzschild‡ and of Epstein.§ Not only have the position and number of the components been accounted for satisfactorily, but the state of polarization and the intensity of the components have yielded to theoretical treatment. Indeed, it may be said that this constitutes one of the most striking successes of the quantum theory.

* Lo Surdo, *Accad. Lincei, Atti*, vol. 22, p. 664, 1913; vol. 23, p. 82, 1914.

† J. Stark, *Preuss. Akad. Wiss. Berlin*, vol. 40, p. 932, 1913.

‡ Schwarzschild, *Preuss. Akad. Wiss. Berlin*, p. 548, 1916.

§ Epstein, *Ann. d. Physik*, vol. 50, p. 498, 1916.

When an electric field $\mathbf{F}$ is applied, the negative energy of an n_k orbit is increased by the amount $\frac{3\mathbf{F}h^2nk}{8\pi^2me}$.

Hence in a transition from this orbit to another orbit defined by the quantum numbers n', k' , there is a change in frequency of amount

$$C(n'k' - nk),$$

where

$$C = \frac{3\mathbf{F}h}{8\pi^2me} \quad \dots \quad 13:22$$

The quantity denoted C , which is proportional to the applied field, may be written in the form

$$C = \frac{3}{a} \frac{\mathbf{F}e}{4\pi mc} \quad \dots \quad 13:23$$

It is interesting to compare this form of the expression with that giving the normal Zeeman resolution which is (Chapter XV)

$$\Delta\nu = \frac{\mathbf{H}e}{4\pi mc} \quad \dots \quad 13:24$$

In equation 13:24 the electron charge is in electrostatic units, but $\mathbf{H}$ is in electromagnetic units.

D. *The Model of Newgass.*

So far as is known no definite suggestion has been put forward associating the "universal" moment of momentum of Sommerfeld with any particular structure or system, which will furnish the correct value for a . G. A. Newgass* has, however, discussed a possible physical interpretation of the relationship between h , c , and e on these lines. He considers the case of two equal charged spheres in contact rotating about the radical axis. Assuming the electromagnetic mass of each sphere to be concentrated at its centre, he obtains an expression for the angular momentum which is independent of the size of the system and is proportional to e^2/c . If this be identified with the quantum of angular momentum $h/2\pi$, a relation between the three fundamental constants considered is obtained, and it is suggested that if the angular momentum of the system were calculated accurately, the relation might be that proposed by Lewis and Adams. The critical angular velocity of rotation is supposed to be that at which the centripetal force would balance the electrostatic attraction between the oppositely charged spheres. It is also suggested that some such electric doublet is the unit of radiation.

* G. A. Newgass, *Phil. Mag.*, vol. 43, p. 698, 1922.

E. *Whittaker's Quantum Mechanism in the Atom.*

In Whittaker's paper on the quantum mechanism in the atom described in Chapter VIII, the quantity $e^2\sqrt{(L/C)}$ is regarded as a natural constant of the dimensions of action, and is equated to h/π . Here L and C denote the inductance and capacity, respectively, of an assumed Hertzian oscillator in the atom. This assumption gives at once

$$\frac{2\pi e^2}{hc} = \frac{2}{c} \sqrt{\frac{C}{L}},$$

which is equivalent to

$$\sqrt{\frac{C}{L}} = \frac{1}{2}ac \quad . \quad . \quad . \quad 13:25$$

According to Whittaker's view, the existence of a natural constant of action simply indicates that the Hertzian oscillators in the atoms are similar to each other in structure and differ only in scale. The constant a may be looked upon as bound up with the structure of the oscillator.

F. *Compton's Theory of X-ray Scattering.*

A. H. Compton* has proposed a quantum theory of the scattering of X-rays by electrons, devised primarily to account for the change in wave-length observed in the scattering of light by free electrons. In dealing with the collision between a light quantum and a free electron, he assumes that the momentum of the former is given by $h\nu/c$, and shows that in virtue of the principles of conservation of energy and of momentum the collision must result in the light quantum recoiling at some angle θ with energy $h\nu_\theta$, which is smaller than $h\nu_0$, the energy at incidence. This means that light should be changed from a higher frequency to a lower by impact with a free electron. A simple calculation shows that the wave-length is determined by

$$\lambda_\theta = \lambda_0 + 2\gamma \sin^2 \frac{1}{2}\theta \quad . \quad . \quad . \quad 13:26$$

where γ is a length given by

$$\gamma = h/mc = 0.0242 \text{ I.A.U.} \quad . \quad . \quad . \quad 13:27$$

This result has been tested experimentally, and it is now generally admitted that the evidence for the reality of the Compton effect is convincing.

Introducing a_1 , the radius of the innermost Bohr orbit of the hydrogen atom, where $a_1 = \left(\frac{h}{2\pi}\right)^2 \frac{1}{me^2}$ we find

$$\gamma = a(2\pi a_1) = a \text{ (circumference of innermost orbit)} \quad 13:28$$

Another way of expressing this quantum length γ is to compare it with the radius of the electron. On the usual assumption that

* A. H. Compton, *Phys. Rev.*, vol. 21, pp. 483, 715, 1923; vol. 22, p. 409, 1923. *Nature*, vol. 112, p. 435, 1923.

the electron may be regarded as an electrically charged sphere $m = \frac{2}{3} \frac{e^2}{rc^2}$ where r is the radius of the sphere. Then $\gamma = \frac{3\pi}{a}r$. The exact value of the numerical factor depends on the assumptions made as to the conditions at the surface of the electron and the shape assigned to it.

G. McLaren's Magneton.

In 1913 McLaren* discussed the angular momentum of the magneton and obtained an expression of a very general character which applies to any magneton of the type he considered. A proof of McLaren's theorem has already been given (p. 41), and it has been shown that in ordinary units the angular momentum of the magneton is $\frac{I}{2\pi} N_m N_e$, where N_m is the number of tubes of magnetic induction linked through its aperture, and N_e the number of tubes of electric induction terminating on its surface, the latter number being here regarded as numerically equal to the charge on the surface. If we identify the angular momentum with Nicholson's value $h/2\pi$ we find

$$N_m N_e = h \quad . \quad . \quad . \quad I3 : 29$$

If further we identify the charge of the magneton with the electron charge, and put $N_e = e$, we find for the magneton in the one-quantum state

$$N_m = \frac{h}{e} \quad . \quad . \quad . \quad . \quad . \quad 13:30$$

This may be taken as defining the strength of the fundamental or quantum tube of magnetic induction.

On combining this result with the expression defining α we obtain

$$a = \frac{2\pi}{c} \frac{N_s}{N} \quad . \quad . \quad . \quad . \quad . \quad 13:31$$

Whether the relation of Lewis and Adams gives the correct value for α or not, it is clear that this number represents one of the most important physical constants. It may be regarded as indicating a deep-seated relation between the ultimate nature of electric force and that of magnetic force. According to a suggestion made to the author by W. H. Watson the constant may be interpreted as giving the relation between a quantum tube of magnetic induction and a unit electrostatic tube of force. We have, however, at present no clear indication as to how the actual value of the constant is to be found theoretically.

* S. B. McLaren, *Phil. Mag.*, vol. 26, p. 800, 1913; *Nature*, vol. 92, p. 165, 1913; *Scientific Papers*, pp. 45, 46, 54 (Cambridge University Press, 1925).

CHAPTER XIV

THE STRUCTURE OF RADIATION

Are not gross Bodies and Light convertible into one another, and may not Bodies receive much of their Activity from the Particles of Light which enter their Composition ?

The changing of Bodies into Light, and Light into Bodies, is very conformable to the Course of Nature, which seems delighted with Transmutations.

SIR ISAAC NEWTON, *Opticks*, Book III, Quest. 30

While many physicists, through conservatism, reject the ideas developed by me, or, at any rate, maintain an expectant attitude, a few authors have attacked them for the opposite reason, namely, as being inadequate, and have felt compelled to supplement them by assumptions of a still more radical nature, for example, by the assumption that any radiant energy whatever, even though it travel freely in a vacuum, consists of indivisible quanta or cells. Since nothing probably is a greater drawback to the successful development of a new hypothesis than overstepping its boundaries, I have always stood for making as close a connection between the hypothesis of quanta and the classical dynamics as possible, and for not stepping outside of the boundaries of the latter until the experimental facts leave no other course open.

MAX PLANCK

There are phenomena from which, if we had to judge by them solely, we should certainly infer that the energy of a quantum not only has a definite amount, but also remains confined to a very small space. In this way one has been led to the idea of "concentrated quanta," which may well be said to be Newton's corpuscles in a modernized form. The phenomena to which I alluded are those of photo-electricity.

H. A. LORENTZ

1. The Nature of Light

IN classical times Greek philosophers discussed the nature of light and proposed various theories which may be regarded as the prototypes of the more modern views. The emission theory, which assumes that a luminous body emits small particles or corpuscles travelling in straight lines through space, is usually associated with the name of Sir Isaac Newton. But Newton himself wrote: "I shall not assume this or any other hypothesis not thinking it necessary . . . yet while I am describing this,

to avoid circumlocution and to represent it more conveniently I shall speak of it as if I assumed it and proposed it to be believed." In 1665 Hooke published a theory according to which light is "a quick and short vibratory motion, propagated in every way through a homogeneous highly elastic medium in straight lines, like rays from the centre of a sphere." But the true founder of the undulatory theory was Huyghens (1678), although his views were not finally accepted till the time of Young and Fresnel. It has been said: "There is no other instance in the history of modern physics in which the truth was so long kept down by authority." The wave theory, firmly established as it appeared to be on an experimental basis, received further support from the work of Maxwell and Hertz, who regarded the waves as electromagnetic disturbances travelling with an assigned velocity. In 1889 Hertz said: "We know the velocity of the waves, we know their lengths, and we know that they are transverse: in short, our knowledge of the motion is complete. A doubt about these things is no longer possible; a refutation of these views is inconceivable to the physicist. The wave theory of light is, from the point of view of human beings, certainty."

And yet, at the present time, the wave theory is in its turn being faced with difficulties. The paradoxical character of the contemporary position lies in the fact that while purely "optical" phenomena, such as interference and diffraction, seem to require some form of undulatory theory, "electrical" phenomena, associated with the emission and absorption of radiation, seem to demand a concentration of the radiant energy in discrete parcels. "Neither the wave nor the quantum hypothesis, in its present form, however, seems to offer any means of explaining the phenomena covered by the other; indeed each hypothesis seems definitely, in many cases, to rule out the possibility of the occurrence of effects which are actually observed." *

2. Light Quanta

The hypothesis of "light quanta" is associated with the name of Einstein (p. 4). According to his view the energy of a quantum of radiation not only has a definite magnitude $h\nu$, but may be regarded as confined to a very small space. Each unit of energy moves outwards without dividing, and can only be absorbed or emitted as a whole. When an electron is liberated under the action of light, the simplest assumption to make is that the whole energy is given to a single electron, so that the electron leaves the body with kinetic energy,

$$\frac{1}{2}mv^2 = h\nu - P \quad . \quad . \quad . \quad 14:1$$

* E. C. Stoner, *Proc. Camb. Phil. Soc.*, vol. 22, p. 577, 1925.

where P is the work the electron has to do in leaving the body. This is Einstein's photo-electric equation, which has now been verified with great accuracy over a very wide range.

This view accounts for the proportionality between the number of electrons emitted and the intensity of the radiation, and for the fact that the energy of the electron is independent of the intensity of the active light, being in fact determined by the frequency of the light.

Silberstein * suggests the term "light dart" as a designation for the quantum of radiation proposed by Einstein, taking the view that though the cross-section of the quantum might be small, there might be considerable length in the direction of propagation, the bundle of radiant energy being imagined as a long train of waves. Lowry † and Silberstein independently have employed the conception of light quanta in dealing with the problem of the latent image on the photographic plate. Some writers employ the term "quant" to denote a light quantum. A more euphonious name has been suggested by G. N. Lewis ‡ in the word "photon," which, however, suffers from the disadvantage of its resemblance to "proton." Lewis regards the photon as "a new type of atom, an identifiable entity, uncreatable and indestructible, which acts as the carrier of radiant energy, and, after absorption, persists as an essential constituent of the absorbing atom until it is later sent out again, bearing a new amount of energy." He postulates certain properties for the photon, including a law of conservation which states that in any isolated system the total number of photons is constant, and discusses objections which may be brought against this idea. The energy of an isolated photon divided by Planck's constant gives the frequency of the photon.

The properties which are assigned to the photon recall the characteristics attributed to quantum magnetic tubes in Chapter XI.

3. Propagation along Lines of Force

J. J. Thomson § has developed an instructive hypothesis as to the action of radiation by assuming that the æther through which the light is travelling has disseminated through it discrete lines of electric force. The energy travelling outwards with the wave

* Silberstein, *Phil. Mag.*, vol. 44, pp. 257, 956, 1922; vol. 45, p. 1062, 1923.

† Lowry, *Phot. Journ.*, vol. 62, p. 193, 1922.

‡ G. N. Lewis, *Nature*, vol. 118, p. 874, 1926.

§ J. J. Thomson, Silliman Lectures at Yale, 1903, *Proc. Camb. Phil. Soc.*, vol. 14, p. 417, 1906-8.

is not spread uniformly over the wave front, but is concentrated in those regions where the pulses are travelling along the lines of force. Thus the front of a Röntgen pulse or a wave of light would suggest the appearance of a number of bright spots on a dark ground. "From this point of view the distribution of energy is very like that contemplated on the old emission theory, according to which the energy was located on moving particles sparsely disseminated throughout space. The energy is, as it were, done up in bundles, and the energy in any particular bundle does not change as the bundle travels along the line of force."

Commenting on this hypothesis Whetham * remarks: "Each tube of force would convey its own tremors, and these would constitute light, but between them would lie undisturbed seas of æther. Such an idea about the nature of a wave-front of light is very unexpected and surprising. We are inclined at once to relegate our tubes of force to a museum of conceptual curiosities. But it is a remarkable thing that certain evidence in favour of the discontinuous nature of a wave-front really does exist."

The conception of the existence of discrete tubes of electric force was made familiar through the earlier writings of J. J. Thomson.† On this question Jeans‡ makes the comment: "These ideas seem to many physicists to be at variance with experience, but they have to their credit that they give a natural and simple explanation of the electrokinetic momentum in the æther such as I believe cannot be given by any other series of physical conceptions." The conception of light as being propagated along Faraday lines of electric force has been employed freely by N. R. Campbell in his textbook on *Modern Electrical Theory* (1913), and he has considered (§ 140) the bearing of the principle of relativity on the problem. He holds that difficulties can be avoided "if the view is taken that the disturbances which are observed by the observer are propagated along the lines attached to the observer's system and not along those attached to the source."

Millikan § has raised two potent objections against what he terms the "æther-string" theory. "The first is that no one has ever yet been able to show that such a theory can predict any one of the facts of interference. The second is that there is direct positive evidence against the view that the æther possesses a fibrous structure. For if a static electrical field has a fibrous

* Whetham, *Experimental Electricity*, p. 207 (1905).

† J. J. Thomson, *Recent Researches in Electricity and Magnetism*, Chap. I (1892); *Elements of Electricity and Magnetism*, p. 279 (1904); and later books.

‡ J. H. Jeans, *Report on Radiation and the Quantum Theory*, p. 81 (1914).

§ Millikan, *The Electron*, p. 229 (Ninth Impression, 1923).

structure, as postulated by any form of æther-string theory, "each unit of positive electricity being the origin and each unit of negative electricity the termination of a Faraday tube," then the force acting on one single electron between the plates of an air condenser cannot possibly vary continuously with the potential difference between the plates. Now in the oil-drop experiments we actually study the behaviour in such an electric field of one single, isolated electron and we find, over the widest limits, exact proportionality between the field strength and the force acting on the electron as measured by the velocity with which the oil drop to which it is attached is dragged through the air.

"When we maintain the field constant and vary the charge on the drop, the granular structure of electricity is proved by the discontinuous changes in the velocity, but when we maintain the charge constant and vary the field the lack of discontinuous change in the velocity disproves the contention of a fibrous structure in the field, unless the assumption be made that there are an enormous number of æther strings ending in one electron. Such an assumption takes all the virtue out of an æther-string theory."

4. Light and Electrons

In an interesting survey of the problems connected with æther and electrons Sir Oliver Lodge* has propounded the question: "Does light generate an electron?" The hypothetical conversion of radiation into matter may, as he points out, accord with observed results as to the photo-electric emission of electrons. In particular the striking reciprocal relation between the energy of an electron and the energy of X-rays seems to justify his statement: "It is as if the same beta particle, that is, the same electron, had gone out of existence at one place, and had been recreated at another, the intermediate link being constituted by specific radiation of a perfectly definite wave-length."

In this connection attention may be directed to a suggestion made by Whittaker in his paper on the quantum mechanism in the atom (page 109). He points out that Bohr's theory of series spectra can be assimilated to his theory in the following way: "In Bohr's theory let a negative electron E fall from an orbit of radius a_1 (position P_1) to an orbit of radius a_0 (position P_0). Now in the initial state of this system, which consists of the electron E at P_1 , let us introduce two coincident electrons E' and E'' at P_0 , one positive and one negative, so that they annul each other; and let us replace Bohr's conception of the fall of the electron from E at P_1 to E' at P_0 by the conception of the dis-

* Lodge, *Nature*, vol. 112, p. 185, 1923.

charge of a condenser whose charges are E and E'' ; the discharge annihilates E and E'' , and so leaves E' surviving alone at the end of the process, and is therefore equivalent to Bohr's notion of a translation of E to the position of E' ."

The suggestion is easier to visualize if instead of the circling electrons of Bohr's theory we employ the stationary electrons obtained by introducing Langmuir's "quantum force." The conception of the discharge of a condenser is not essential to the picture, and may, if it be preferred, be replaced by a vibration of the column of æther between P_1 and P_0 , resulting in the production of a "light dart," or by the formation of an electric vortex ring as in Thomson's theory. In either case we are using figurative language, which is meant only to suggest an illustration of a process which is at present beyond the range of our experience.

One of the difficulties in Bohr's theory is to understand how the frequency of the radiation emitted in accordance with his fundamental frequency condition can be fixed as soon as the electron quits the first stationary state and before it has reached the final state. As Silberstein expressed it in 1920: "Needless to say the founder of the new theory and his followers do not attempt to describe the mechanism of such an extraordinary performance, one, that is, that enables the atomic system to hit precisely upon the frequency required." Again, C. G. Darwin has referred to the difficulty "that the quantum conditions determining the permissible Bohr orbits can only be explained physically by attributing to the electrons a knowledge of the future."

This difficulty—and the similar one which arises in connection with absorption—seems to be diminished, if not entirely removed, by Whittaker's suggestions. On this view the emission of light originates not so much at the position P_1 as at the position P_0 .

Reference may be made here to the alternative picture put forward in the chapter dealing with quantum magnetic tubes in rotation. There it was suggested that a closed tube of magnetic induction, according to the rotation imposed upon it, might play the part of either a positive or negative electron or (when not in rotation) of a light-quantum.

"If we take it for granted that light and electromagnetic disturbances are propagated either by or through a medium of some sort, the question naturally arises whether the substance of which this medium is composed is essentially different from the substance which is commonly associated with the elementary electrified particles or electrons." H. Bateman has discussed this problem, starting with the simple hypothesis that there is one primeval substance (which may be called electricity) from which both matter and æther are built up. He finds that in certain cases "a moving line of electric force is always composed

of the same particles of electricity" and "a moving line of magnetic force always consists of the same particles of electricity." These ideas are related to the later work of J. J. Thomson and of Whittaker, which we now proceed to consider.

5. The Electric Ring Quantum

An interesting development of the idea of propagation of light along a tube of electric force was given by J. J. Thomson* in 1924. In considering the structure of light, he suggested "a mental picture based on the idea of tubes of electric force" which might be found useful in reconciling the optical effects of light with its electrical properties. He assumes the mutual potential energy of an electron and a positive charge to be located in the tube of force joining them. When the electron falls from a point P_1 to a point P_0 nearer the positive charge this potential energy is diminished by the energy in the portion P_1P_0 of the tube. We may picture the energy in this portion of the tube as getting free by supposing that the tube is thrown into a loop during the motion of the electron: the two sides of the loop approach each other; and the closed part of the loop gets detached and goes off as a closed ring. This ring rapidly becomes circular and travels with the velocity of light in a direction at right angles to its plane, like a circular vortex ring.

Exactly the reverse process may be supposed to take place when the ring gives up its energy to some other tube of force. It may be that the additional energy given to the tube in this way is large enough to detach the electron concerned from its positive charge. A free electron is then produced and the ring disappears.

There is an alternative possibility, namely that the energy, though not large enough to detach the electron from the atom, is sufficient to bring it into another position of equilibrium. When the electron falls back to its old position, a new ring will be formed and a quantum of radiation emitted.

The energy of the ring is given by the formula:

$$E = 8\pi^2 p^2 e^2 \frac{r^3}{b^2} \frac{1}{2\pi r} \quad \dots \quad \text{14:2}$$

where r is the radius of the ring, b the radius of the cross-section, and p a number not greater than unity (p would be equal to unity if all the lines of force from the electron were done up in one bundle). Assuming that all rings are geometrically similar, their energy will be proportional to $1/r$.

The energy of the ring may be supposed to conform to the relation $E = h\nu$ and we may, for convenience, assume that the

* J. J. Thomson, *Phil. Mag.*, vol. 48, p. 737, 1924.

time of vibration of the ring is the time taken by light to travel round the circumference, so that $\nu = c/2\pi r$. Then

$$E = 8\pi^2 p^2 e^2 \frac{r^2}{b^2} \frac{\nu}{c} \quad . \quad . \quad . \quad 14:3$$

This means that we must put

$$h = \frac{8\pi^2 e^2}{c} \left(\frac{pr}{b} \right)^2 \quad . \quad . \quad . \quad 14:4$$

Approximate numerical agreement may be obtained by supposing that $pr/b = \pi$.

The model may be employed, as J. J. Thomson has shown, to give an account of the absorption of light and also of the effect of resonance. The waves round the ring are also considered, and the results utilized for the explanation of interference. "To sum up, light on this view is made up of units, each of which contains a core in which the energy is concentrated; this core is surrounded by a system of electric waves which, though they have but little energy, give rise in cases where diffraction or interference occurs to electric and magnetic forces which deflect the paths of the cores without altering their energy. The core is supposed to vibrate in a definite period, and this period coincides with that of the electrical waves which surround it."

It may be recalled that in a previous chapter a light quantum was pictured as a closed tube of magnetic induction. The point that distinguishes Thomson's theory is that he pictures the quantum as a closed tube of electric force. Probably a more correct picture would be obtained by combining these two views. To H. Bateman is due the credit of having first constructed fields which satisfy exactly the Maxwell-Lorentz equations, and are propagated without spreading. Whittaker * has put forward a justification of Thomson's hypothesis, and shown how it may be brought within the compass of an extended form of the Maxwell-Lorentz theory.

Whittaker first comes to the conclusion that the lines of electric force in a light quantum must be closed curves in planes perpendicular to the direction of propagation, and then points out that a closed line of electric force cannot exist unless a "magnetic current" is passing through the aperture formed by it. There seems no escape from the conclusion that magnetic currents are involved necessarily in Thomson's assumption of closed lines of electric force. This requires a modification in the Maxwell-Lorentz equations, for we must now introduce the volume density of the "magnetism" whose convection constitutes the magnetic current. So long ago as 1885 Heaviside † intro-

* E. T. Whittaker, *Proc. Roy. Soc. Edin.*, vol. 46, p. 116, 1926.

† Heaviside, *Electrician*, p. 306, Feb. 21, 1885.

duced into Maxwell's equations terms representing a magnetic conduction current, and in 1922 Whittaker, as we have seen in Chapter VIII, employed the idea of "magnetic currents" in his quantum mechanism in the atom. Lorentz * has remarked that the Maxwell-Lorentz equations with these additional terms "form a consistent system and are in good agreement with ideas and theorems which physicists would be very unwilling to give up."

The analytical construction of the field of the light quantum is described by Whittaker as follows. The axis of x is taken parallel to the direction of propagation and the disturbance is supposed wholly confined to the region inside a cylinder of radius a , whose axis is the axis of x . The components of the electric force within the cylinder are assumed to be

$$E_x = 0, \quad E_y = -z(a - r)f(x - ct), \quad E_z = y(a - r)f(x - ct) \quad 14:5$$

These equations give at once

$$\frac{E_x}{0} = \frac{E_y}{-z} = \frac{E_z}{y} \quad . \quad . \quad . \quad 14:6$$

showing that the lines of electric force are circles with their centres on the axis of x and their planes perpendicular to this axis. The factor $f(x - ct)$ secures that the field travels parallel to the axis of x with the velocity, c , of light.

The components of the magnetic force within the cylinder are found to be

$$H_x = 0, \quad H_y = -y(a - r)f(x - ct), \quad H_z = -z(a - r)f(x - ct) \quad 14:7$$

The magnetic vector is everywhere at right angles to the electric vector as in ordinary waves of light.

As the assumption of closed lines of electric force implies the existence of "magnetic currents," it is necessary to assume the existence of "magnetism" within the pulse, although when we speak of "magnetism" as "existing" at a place, we really assume no more than that the magnetic vector is not solenoidal there. Denoting by μ the volume-density of the "magnetism," Whittaker finds

$$\mu = -(2a - 3r)f(x - ct) \text{ when } r < a \quad . \quad . \quad 14:8$$

It is easily shown that the total quantity of magnetism in the pulse is zero.

In the experiments of C. T. R. Wilson † and of F. W. Bubb ‡ photo-electrons were ejected by a plane-polarized beam of X-rays and the results indicated that the electron received an impulse forwards (in the direction of propagation) together with a sideways impulse in the direction of the electric vector. This suggests

* Lorentz, *Proc. Amsterdam Acad.*, vol. 25, p. 414, 1923.

† C. T. R. Wilson, *Proc. Roy. Soc. A*, vol. 104, p. 1, 1923.

‡ F. W. Bubb, *Phys. Rev.*, vol. 23, p. 137, 1924.

that the light quantum is itself polarized. It has been shown by J. M. Whittaker * that such a polarized light quantum may be constructed analytically on the basis of the extended Maxwell equations employed by E. T. Whittaker. The lines of electric force form closed curves and over the greater part of the quantum are nearly parallel to one direction. The form of these lines suggests that this plane-polarized light quantum might be formed by the coalescence of two-ring quanta, circularly polarized in opposite senses.

J. M. Whittaker has also discussed the important question of the way in which the frequency enters into the expression for the quantum. His conclusion is that when referred to cylindrical co-ordinates, r, θ, x , the equations defining the ring quantum take the final form

$$\left. \begin{aligned} H_r &= -E_\theta = -r(a-r)\nu f\left\{\nu\left(t-\frac{x}{c}\right)\right\}; \\ H_\theta &= E_r = H_x = E_x = 0 \\ \mu &= (3r-2a)\nu f\left\{\nu\left(t-\frac{x}{c}\right)\right\} \end{aligned} \right\} (r < a) \quad \text{14:9}$$

$$\text{All} = 0 \quad \dots \dots \dots (r > a)$$

The energy in this quantum is found to be $h\nu$ where

$$h = \frac{\pi a^3 c}{30} \int_{-\infty}^{\infty} [f(u)]^2 du \quad \dots \dots \dots \text{14:10}$$

a constant the same for all quanta of the same "shape" but different frequencies, since a is the same for all such quanta.

It may be of interest to suggest at this point the possibility of obtaining a relation between the quantum and the electron. It seems natural to assume that the ring of electric force may be derived from a line of force connecting a positive and negative electron. Let us therefore put for the electron charge

$$e = \int_0^a \int_{-\infty}^{\infty} E_\theta dr dx \quad \dots \dots \dots \text{14:11}$$

Then in the previous notation we find

$$e = \frac{a^3}{6} \int_{-\infty}^{\infty} \nu f\left\{\nu\left(t-\frac{x}{c}\right)\right\} dx$$

that is

$$e = \frac{a^3 c}{6} \int_{-\infty}^{\infty} f(u) du \quad \dots \dots \dots \text{14:12}$$

So the value of the constant a employed in Chapter XIII is

$$a = \frac{2\pi e^2}{hc} = \frac{20\pi}{3} \left[\int_{-\infty}^{\infty} f(u) du \right]^2 \div \left[\int_{-\infty}^{\infty} [f(u)]^2 du \right] \quad \text{14:13}$$

* J. M. Whittaker, *Proc. Roy. Soc. Edin.*, vol. 46, p. 306, 1926.

By a suitable choice of the arbitrary function $f(u)$ it may be possible to obtain the right numerical value for α .

6. A Magnetic Light Quantum

Whittaker* has described a simple light quantum which is a solution of Maxwell's equations, and therefore behaves in accordance with the classical theory as regards refraction, interference and polarization. But it has the property that when it encounters an atom, at any distance, however great, from the source, in certain cases *the whole* of its energy will be absorbed by the atom.

A magnetic doublet AB containing a positive magnetic charge m at B, and a negative charge $-m$ at A will set up a magnetic field extending over all space. When this magnetic molecule is set in motion in the direction Ox at right angles to AB, the magnetic attraction between the charges at A and B will be diminished by the electromagnetic force due to the motion, and



FIG. 25.—Moving Magnetic Doublet.

when the molecule is moving with the velocity of light these forces balance, and we no longer need any material framework to keep the two charges apart. We can indeed suppose the charges completely disembodied.

When the molecule is in motion the lines of magnetic force concentrate towards the plane through O perpendicular to Ox ; in the limit when the velocity is that of light, the lines of force are confined entirely to this plane. There will be lines of electric force everywhere perpendicular to these lines of magnetic force. The original magnetostatic field has become a plane wave of light by merely setting it in motion with the velocity of light.

This plane wave, however, differs from the plane wave of light usually considered. The intensity of the disturbance is not the same over the whole of the infinite plane wave-front, but diminishes as we go outwards from O, and is zero at infinity. In the second place, the wave has a singularity at O, representing the disembodied form of the magnetic molecule. Whittaker calls this singularity the "speck" on the wave-front, and points out that it confers on the wave the desired "quantum" properties. The "speck" retains the property of being acted on by mag-

* E. T. Whittaker, *Phil. Mag.*, vol. 2, p. 1137, 1926.

netic forces, and by electric forces also, and should it pass very near to an atom, there is a possibility that it may be attracted into the atom, and the *whole* of the energy will now have become the property of the atom. The energy may be partly located in the space outside the atom, but it belongs to the atom, in the sense that wherever the atom moves, this bundle of energy moves with it. Thus Einstein's theorem that every parcel of light-energy which is emitted from an atom is ultimately entirely absorbed by a single other atom is here seen to be a consequence of the strict classical electromagnetic theory of light.

7. Interference and the Light Quantum Hypothesis

Stoner* has discussed the question of interference and inquired what sort of modifications in outlook are necessary, or what additional properties of radiation must be postulated, in order that interference and allied phenomena may be explained on the basis of the existence of light quanta. It must be assumed that the quantum of radiation has periodic properties, so that it varies periodically in some way as it travels through space. This leads to the introduction of a quantity analogous to wave length, although the adoption of the quantum hypothesis involves abandonment of the wave picture. The "wave length" may be defined as the least distance between two points at which the quantum has the same characteristics; the "period" as the time between two returns to the same state, and the "frequency" as the inverse of this. The idea of the "phase" of a quantum may also be introduced, a measure of it being given by the time which has elapsed since the quantum was in some arbitrarily defined state.

"A wave theory can account admirably for the production of interference fringes; but to explain interference it is necessary to do more than this; it is necessary to correlate the observed intensity at different points of a fringe system with the numbers of quantum switches induced by the radiation. Maxima and minima of fringe systems must ultimately be regarded as points at which the greatest and least number of quanta are actually absorbed (or absorption switches induced), and not merely as points passed by a greater or lesser number of quanta.

"A single quantum could not produce a fringe system, yet the idea that this is possible lies at the root of the gravest objection to light quanta. 'The bright and dark fringes to which it [a beam consisting of separate quanta] gives rise,' Lorentz says, 'could never be sharper than those that would be produced by a single quantum.' The picture of a single quantum producing a fringe system over which there is a variation in the total

* E. C. Stoner, *Proc. Camb. Phil. Soc.*, vol. 22, p. 585, 1925.

number of whole quanta absorbed is purely fantastic, and perhaps points out a direction of possible escape from difficulties.

“An explanation of interference must be sought in the joint action of different quanta, and not in the properties of a single one. Experimentally, interference fringes are observed when radiation reaches the point of observation by different paths from a ‘single point’ source. It is important to notice that interference effects do not depend for their appearance on the light originating from a single emitting source, say a single atom. The phase relations necessary are apparently satisfied if the light can be supposed to emanate from a ‘geometrical point’; there seems to be no evidence that the physical structure of the point (that is the actual emitting systems) must remain constant even over periods comparable in time with the duration corresponding to the coherence length of the wave trains emitted (as is shown in a special case by Thomson’s experiment). Though the reason may thus be obscure, even on orthodox classical consideration, from a wave standpoint, the single point source ensures that there shall be some definite phase relation between the interfering wavelets. To account for interference properties there must be some corresponding relation for different quanta originating at the same point. It seems not unnatural or far-fetched to assume that their phase at the point of origin is the same—that the ‘phase at emission’ for similarly polarized quanta, at least, is constant, and hence that different quanta travelling by two paths arrive at a point of observation in the same phase if the path difference is a whole number of ‘wave lengths’ as above defined.

“To ‘explain’ interference, however, a further assumption is necessary. It must be supposed that a quantum in a given phase passing an absorbing system, say an atom, tends to modify it (by orientation or otherwise) in such a way as to increase its probability of absorbing a quantum in that phase. It is assumed, in other words, that for absorption to occur, ‘coupling’ must take place between the absorbing system and the quantum; this ‘coupling’ requires a definite relation between the phase of the quantum and the state of the system; and the passage of a quantum gives the system a definite impulse towards the state corresponding to its own phase. Thus the greater the number of quanta in the same phase which pass an absorbing system, the greater the probability of absorption of one of them; the passage of quanta of opposite phase, producing opposite impulses, will diminish the probability of absorption. It must of course be supposed that the effect of the impulse persists, unless the state is modified by external disturbances, for Taylor’s classical experiment shows that interference effects still occur even for very weak light.”

Thus there seems a possibility of explaining interference on a light quantum basis by attributing phase properties to quanta, and to absorbing systems states corresponding to these phases. It may be assumed further that in the reaction between an atomic system and a quantum, the system is given an impulse, whose effect persists, towards the state corresponding to the phase of the quantum.

8. Experimental Evidence for Light Quanta

The arguments in favour of the view that the quantum of monochromatic radiation emitted from an atom in accordance with Bohr's frequency relation travels linearly have been forcibly stated by Stoner.

"A simple consideration of photo-electric absorption seems to provide a very cogent argument in favour of linearly directed quanta. In complete accord with electromagnetic theory, and relativity, experiments on the pressure of radiation have shown it to be statistically true that absorption of radiant energy E is associated with transfer of momentum E/c . According to modern views all absorption of radiant energy takes place by quanta $h\nu$, and it seems difficult to escape the conclusion that this process is associated with transfer of momentum $h\nu/c$. Actually this association is only known experimentally to be true for a large number of switches; if in some switches less momentum is transferred, in others more must be. Now for waves with energy E the total associated momentum varies from zero for spherical waves to a maximum of E/c for plane waves. Unless some artificial means of increasing this maximum is devised, it seems, therefore, that all absorption corresponds to absorption of plane waves—in other words, since absorption takes place only by quanta, that quanta are linearly directed."

In recent years evidence in favour of the actual reality of light quanta has accumulated. Not only has the experimental evidence in favour of Einstein's photo-electric law become more exacting in its quantitative demands, but the results of A. H. Compton and others on the change of wave-length of scattered X-rays are difficult to explain without using in some form the conception of a concentrated unit of radiant energy. Further, there is increasing evidence that photochemical and photographic actions are intimately related to absorption of quanta of amount $h\nu$.

Compton's theory (arrived at independently by Debye) receives support from experiments by Simon and Compton* in

* A. H. Compton, *Proc. Nat. Acad. Sci.*, Washington, vol. 11, No. 6, p. 303, June, 1925.

which stereoscopic photographs were taken, using Wilson's cloud expansion apparatus. In the majority of photographs showing a recoil electron and a secondary β ray track produced by the scattered X-ray quantum, the tracks are in accordance with the prediction of the theory. "The evidence is thus against any spreading wave theory of radiation, which requires that there should be no correlation between the direction of the recoil electron and that of the effect of the scattered quantum."

An experiment by Bothe and Geiger * indicates that the recoil electron, and the photo-electron emitted by the scattered radiation, appear simultaneously. Bennett, using two point counters, one to receive the recoil electron and the other the scattered quantum, finds many simultaneous impulses.

These experiments seem to show the characteristic properties of corpuscles: the localization of the active power of a light wave in space, and in time.

In 1924 Slater † proposed to make a new assumption in quantum theory to the effect that the atom, even before a process of transition between two stationary states takes place, is capable of communicating with distant atoms through a *virtual* radiation field. This idea forms the basis of a joint paper by Bohr, Kramers and Slater ‡ in which an attempt is made to arrive at a consistent description of optical phenomena by connecting the discontinuous effects occurring in atoms with the continuous radiation field in a way somewhat different from that hitherto followed.

The interest of this theory is mainly historical. It has, however, led to a development which is worthy of mention.

Discussing the results in favour of light quanta, Slater § now advocates the view of a virtual radiation field to guide corpuscular quanta, a view which had also been suggested by Swann, || who postulated the existence of a field, obeying Maxwell's equations, the function of which should be to guide the light corpuscles, which might travel along Poynting's vector. Slater assumed the emission of the field before the ejection of the corpuscle; that is, during the stationary state before the transition. ¶ By this device were avoided the difficulties of explaining coherence, of the "size of quanta," of the presence of interference phenomena in weak light.

* Bothe and Geiger, *Zeits. f. Physik*, vol. 32, p. 639, 1925.

† J. C. Slater, *Nature*, vol. 113, p. 307, 1924.

‡ Bohr, Kramers and Slater, *Phil. Mag.*, vol. 47, p. 785, 1924.

§ J. C. Slater, *Nature*, vol. 116, p. 278, 1925.

|| Swann, *Science*, vol. 61, p. 425, 1925.

¶ Compare the suggestion on p. 148 of the presence of magnetic tubes having the same frequency as the radiation before the quantum transition occurs.

9. Angular Momentum in Radiation Processes

The hypothesis of linearly directed, spatially localized light quanta is strongly supported by the experiments which confirm the quantum theory of scattering put forward independently by Compton and by Debye. As we have seen, the properties of the light quantum may be related to the assumption that the principles of conservation of energy and of momentum may be applied to *individual* processes of emission and absorption. In the emission of radiation the atom loses energy and momentum, and these are supposed to appear in the light quantum. Again, it may be supposed that the quantum possesses angular momentum which may assume certain values.

The correlation of changes in angular momentum of the emitting system with observed states of polarization has been considered by Rubinowicz, Sommerfeld and Bohr, and has been developed in detail by these writers and others. The following discussion is due mainly to Stoner (*loc. cit.*):

On the classical theory the total change in the angular momentum ΔP in the radiation field associated with a vibrating electron is related to the change in energy ΔE due to emission or absorption in a manner which varies according to the mode of vibration of the electron from

$$\Delta P = \frac{\Delta E}{2\pi\nu} \quad \text{I4 : I4}$$

for an electron making a circular vibration, to

$$\Delta P = 0 \quad \text{I4 : I5}$$

for an electron vibrating linearly. Carrying this over to the quantum theory, in which ΔE must be put equal to $h\nu$, it is supposed that the angular momentum associated with a quantum may vary from the value $h/2\pi$ (the unit) to the value 0. The former value is supposed to correspond to circularly polarized light, the latter to linearly polarized light. We might have expected to find intermediate values corresponding to elliptically polarized light, but from the study of the Zeeman effect "the rather surprising fact seems to emerge that radiation is not emitted corresponding to that which, classically, an electron moving in an ellipse would produce." "It would seem that there must be quanta of two essentially distinct types corresponding to circular ($\Delta m = \pm 1$) and linear ($\Delta m = 0$) polarization."

Consider now an emission process (uninfluenced by external fields) in which the initial and the final electron orbit are in the same plane and the azimuthal quantum number changes by unity. The emitting system loses unit angular momentum, and we may assume that this momentum is associated with the quantum emitted. Now observations on the Zeeman effect show that the

type of polarization of the emitted light depends on the direction of observation, that is, on the direction of emission relative to the planes of the two orbits involved. From this it would seem to follow that the polarization depends not on the absolute magnitude of the angular momentum associated with the localized quantum, which is possibly always unity, but on its resolved magnitude in, or at right angles to, the direction of propagation.

This conception clears up some of the difficulties which have beset the consideration of absorption.*

An absorption transition of the normal type, the inverse of the emission transition, involves also a change in the azimuthal quantum number by unity; and this can occur, without any breakdown of conservation laws, whatever the polarization of the quantum, provided the absorbing system is suitably orientated.

It seems probable that conservation principles, with reference to angular momentum, will hold also in more complicated transitions such, for example, as occur in the presence of external fields.

The importance of orientation in connection with absorption becomes clear from an examination of the experiments of Wood and Ellett † and others, on the effect of magnetic fields on the polarization of resonance radiation. An analysis of their results shows that certain absorption transitions may be entirely prevented by appropriate orientations of the magnetic fields. The probability of quanta in a definite state of polarization being absorbed thus depends essentially on the orientation of the absorbing system.

The experiments on mercury vapour suggest strongly that absorbing systems may be orientated by the influence of a beam of radiation traversing them.

Stoner goes on to point out that while orientation phenomena seem to be primarily magnetic in character, it may be necessary to consider also an electric vector characterizing an electron orbit, the axial direction of this vector being given by the line joining the "electric centre of gravity" of the orbit to the nucleus of the atom. It seems as if this electric vector may have an importance equal to that of the magnetic vector.

Stoner emphasizes the point that it is possible to associate with the light quantum not only an angular momentum, but also a magnetic moment. This suggestion is definitely in favour of some such model of the quantum as that given by Whittaker. In this connection an interesting point is the relation of the

* Bohr, *On the Application of the Quantum Theory to Atomic Structure*, p. 41, 1924.

† Wood and Ellett, *Proc. Roy. Soc.*, vol. 103, p. 396, 1923; *Phys. Rev.*, vol. 24, p. 243, 1924. See Joos, *Phys. Zeits.*, vol. 25, p. 130, 1924.

polarization of light to the photo-electric effect. In the "selective effect," the value of the photo-electric current may be multiplied many times by changing the plane of polarization. It might be imagined that this is due to the absorption of light polarized in one plane being greater than that of light polarized in another; but while the optical absorption may differ by a factor of 2 or 3 to 1, for the two planes of polarization, the photo-electric emission may differ by 40 or 50 to 1. Thus the undulatory theory does not provide a solution of this problem. On the other hand, though it may not be easy to give a complete explanation in terms of the quantum theory, the conception of a polarized light quantum, which is necessitated by other phenomena, may be invoked here also.

10. The Theory of de Broglie

A tentative theory of light quanta has been put forward by Louis de Broglie* in which it is assumed that (1) the "mass at rest" of every light quantum has a given value m_0 , (2) the velocity v cannot be discriminated from Einstein's limiting velocity c by any experimental means, (3) the frequency is connected with the whole energy of a quantum by the relation:

$$hv = \frac{m_0 c^2}{\sqrt{1 - \beta^2}}, \text{ where } \beta = v/c \quad . \quad . \quad 14:16$$

It appears that m_0 should be at most of the order of 10^{-50} gram. The light quantum must have an internal binary symmetry corresponding to the symmetry of an electromagnetic wave and defined by some axis of polarization.

It is shown mathematically that the Lorentz-Einstein transformation joined with the quantum relation leads us to associate motion of body and propagation of wave. Accordingly de Broglie supposes that any body moving with regard to an observer with velocity $v = \beta c$ ($\beta < 1$) is accompanied by a wave of frequency ν , which spreads with velocity $c/\beta = c^2/v$. This wave, however, according to Einstein's ideas, does not carry energy. A group of waves whose frequencies are very nearly equal has a group velocity which in the usual theory is the velocity of "energy propagation." It is suggested that the velocity of the moving body is the energy velocity of a group of waves having frequencies determined by the above equation and velocities c/β corresponding to very slightly different values of β .

In accordance with the principle of energy inertia, any body of mass m_0 must contain energy of amount $m_0 c^2$. The quantum relation suggests that this internal energy may be ascribed to some periodic phenomenon of frequency ν_0 given by $h\nu_0 = m_0 c^2$. It

* de Broglie, *Phil. Mag.*, 47, p. 446, 1924.

can be shown that if, at the beginning, the internal phenomenon is in phase with the wave, this harmony of phase will always persist.

This idea may be employed to give a physical interpretation of Bohr's analytical stability conditions, for it suggests that the motion of an electron in its trajectory can only be stable if the phase wave is tuned with the length of the path.*

Of all the hypotheses put forward to reconcile the wave and the emission theories of light that of de Broglie is in many respects the most interesting and suggestive. On this view the waves from a source spread out in all directions and the light quantum tends to follow the normal to the wave-surface. Thus the quanta, moving with a speed slightly less than that of light, are constrained to follow paths which will satisfy the requirements of interference.

It may be possible in some such way as this to save both the corpuscular and the undulatory characters of light, and by means of suitable hypotheses a plausible explanation may perhaps be given of coherence and of interference fringes. In the words of de Broglie: "When an atom emits a light quantum, a spherical phase wave is simultaneously emitted and, crossing over the neighbouring atoms of the point source, will excite other emissions. The non-material phase-wave will carry many little drops of energy which slide slowly upon it and whose internal phenomena are coherent."

Starting with the assumption that black-body radiation consists of discrete light-atoms, each having energy $h\nu$ and momentum $h\nu/c$ so that the pressure per unit of boundary surface is $\frac{1}{3}n h\nu$, n being the number of atoms in unit volume, de Broglie † has derived Wien's law of radiation by the methods of statistical mechanics. To obtain the correct numerical factor which is twice that found theoretically, he adopts a suggestion of Brillouin that each light-atom is associated with an internal state of right- or left-handed circular polarization.

H. A. Lorentz esteems the theoretical significance of the *energy fluctuations* of so much importance that he expects to find here the key of the whole radiation problem. Supposing the mean energy E of a system to be known as a function of the absolute temperature T , statistical mechanics supplies an expression for the mean square of the energy fluctuations Δ .

$$\bar{\Delta}^2 = kT^2 \frac{dE}{dT} \quad \text{14:17}$$

where k is Boltzmann's constant. Here Δ represents the devi-

* A similar suggestion has been discussed by G. P. Thomson who supposes that the vibrations in the tube of force connecting electron and nucleus are in tune with the period of the orbit. *Phil. Mag.*, vol. 50, p. 163, 1925.

† L. de Broglie, *J. de Physique et le Radium*, vol. 3, p. 422, 1922.

ation from its mean value E of the instantaneous value of the energy contained in volume V within the frequency interval ν and $\nu + d\nu$.

Assuming Planck's law of radiation in the form

$$E = \frac{8\pi h\nu^3 V d\nu}{c^3(e^{h\nu/kT} - 1)},$$

we find

$$\bar{\Delta}^2 = h\nu E + \frac{c^3 E^2}{8\pi\nu^2 d\nu V} \quad . \quad . \quad . \quad 14:18$$

as Einstein showed in 1911.

Every hypothesis as to the structure of radiation must be in accord with this equation. The second term on the right corresponds to the entirely electromagnetic Rayleigh-Jeans radiation. The first term corresponds to an entirely quantized radiation, for if we assume that the energy of vibration frequency ν is concentrated in discrete independent quanta of magnitude $h\nu$, we find by analogy with the case of an ideal gas:

$$\bar{\Delta}^2 = h\nu E \quad . \quad . \quad . \quad 14:19$$

But this expression agrees with the previous one only in the region within which Wien's law is valid. Consequently, this form of the light quantum hypothesis must be rejected as too restricted. Einstein later introduced certain hypotheses as to the emission and absorption of light quanta which lead to Planck's formula, and therefore may be expected to yield the exact fluctuation law. L. de Broglie* has also discussed the problem and suggested the existence of agglomerations of "light-particles" which may be regarded as forming a gas composed of molecules and atoms. On this basis it is possible to deduce the exact law. He supposes that interference phenomena are associated with the existence of agglomerations of light atoms whose movements are not independent but coherent.

A possible connection between the wave-theory of matter and electromagnetism has been pointed out by H. Bateman.† In de Broglie's theory a particle of matter travelling with velocity v has associated with it a phase-wave travelling with velocity c^2/v . This theory may be related to J. J. Thomson's theory of moving lines of force by interpreting v as a velocity of the electric line and c^2/v as the velocity of the magnetic line.

In conclusion it may be suggested that just as Schrödinger has removed many of the difficulties of ordinary mechanics by introducing his undulatory mechanics, so it may be possible to extend the ideas of de Broglie as applied to radiation and ultimately to reconcile the light quantum hypothesis with the undulatory theory of light.

* L. de Broglie, *Comptes Rendus*, vol. 175, p. 811, 1922.

† H. Bateman, *Nature*, vol. 118, p. 839, 1926.

CHAPTER XV

THE ZEEMAN EFFECT

Thus is established . . . a true, direct relation and dependence between light and the magnetic and electric forces ; and thus a great addition made to the facts and considerations which tend to prove that all natural forces are tied together, and have one common origin.

FARADAY, *On the Magnetization of Light and the Illumination of Magnetic Lines of Force* (Par. 2221)

1. The Discovery of Zeeman and the Classical Explanation

FARADAY'S last experimental work in 1862 was on the relation between magnetism and light. Having previously discovered the rotation of the plane of polarization of light travelling along the lines of magnetic force through certain substances placed in a magnetic field he now sought, but in vain, to detect any change in the lines of the spectrum of a flame when the flame was acted on by a powerful magnet.

The effect looked for by Faraday was discovered in 1896 by Zeeman* at the University of Leiden. He found that the D-lines from a sodium flame were distinctly widened when a strong magnetic field was applied in the space occupied by the flame. A similar result was found in the absorption spectrum of sodium vapour. These results were communicated to H. A. Lorentz, who at once pointed out how the effect might be calculated by means of his electron theory, and predicted that the edges of the modified lines ought to be circularly polarized. This prediction was shortly afterwards verified by Zeeman.

In the first instance we shall consider only the simplest type of the effect, and here we must distinguish between two cases—when the ray is perpendicular to the lines of magnetic force, and when the ray is in the direction of these lines. The classical theory of this action given by Lorentz leads to the conclusion that the *transversal effect* in which the light is emitted in a direction perpendicular to the lines of force, gives rise to the *Zeeman normal triplet*: the *longitudinal effect*, in which the light is emitted parallel to the lines of force, gives rise to two circularly polarized components, the *Zeeman doublet*.

* Zeeman, *Akad. Amsterdam*, vol. 5, pp. 181, 242, 1896; translated in *Phil. Mag.*, vol. 43, p. 226, 1897.

The observed resolution is shown diagrammatically in Fig. 26. The single line at the top of the diagram represents the original unresolved line. Below this are the two lines seen when the source is observed in the direction of the lines of magnetic force. As indicated in the diagram these lines are circularly polarized, but in opposite senses. At the bottom of the diagram is seen the normal triplet; the central component is undisplaced, and the other two are displaced by an amount $\Delta\nu$, occupying the same position as the lines of the Zeeman doublet. All three lines are plane-polarized, the central line with the electric vector parallel to the field, the outer lines with the electric vector perpendicular to the field.

In the normal case the resolution predicted by the theory of

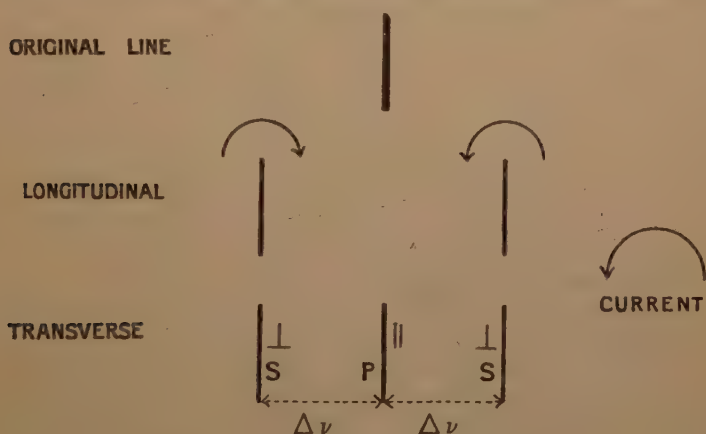


FIG. 26.—Normal Zeeman Resolution.

Lorentz is proportional to the magnetic field $\mathbf{H}$ and amounts to

$$\Delta\nu = \frac{e}{m_0} \frac{\mathbf{H}}{4\pi c} \quad . \quad . \quad . \quad . \quad 15:1$$

If e is in E.S.U. and $\mathbf{H}$ in E.M.U., $\Delta\nu$ will be a frequency in sec.^{-1} . If e is in E.M.U. and $\mathbf{H}$ in E.M.U., then $\Delta\nu$ will be expressed in wave-numbers, cm.^{-1} .

Before taking up the theory in detail it may be mentioned that in the case of multiple lines *anomalous* Zeeman effects are observed. Instead of splitting into three components, the line sometimes splits into a greater number. For these complex resolutions Voigt has given a theory which gives at least a qualitative account of the facts in the case of absorption spectra. Sommerfeld has modified this theory and discussed also the case of emission. Ritz has applied to these problems his atomic model in which an electron describes an orbit in the magnetic

field due to a number of collinear magnetic molecules. An account of his work and of the other early investigations is to be found in Zeeman's *Magneto-optics* (1913).

The normal Zeeman resolution may be deduced by decomposing the motions of the electrons in the atoms into three simple motions: a vibration parallel to the lines of force—this component will be unaltered by the magnetic field—and two circular motions in opposite senses in planes normal to the lines of force. This mode of resolution is legitimate if we assume the motion of the electron to be harmonic.

Take a set of right-handed rectangular axes, OX , OY , OZ , as in Fig. 27. Let us suppose that there is a magnetic field of strength H in the direction of the axis of Z . The motion of the radiating electron is to be decomposed into a linear vibration

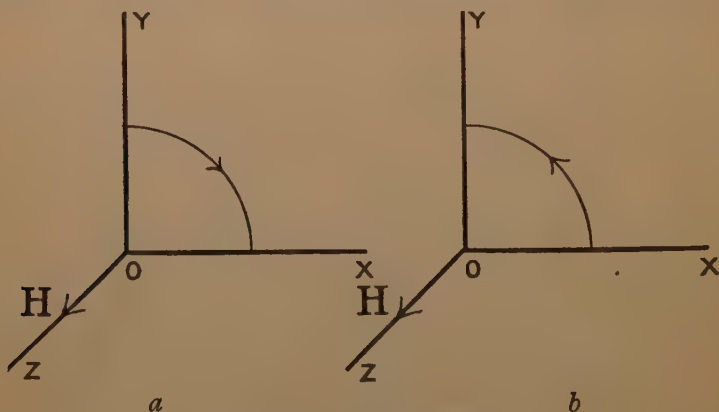


FIG. 27.—Zeeman Effect.

along OZ and two circular motions perpendicular to OZ , i.e. parallel to the plane of XY . These circular motions are in opposite directions (a and b). This resolution is clearly shown in a model constructed by Zeeman and illustrated in his book *Magneto-optics*. The central rod (Fig. 28) is parallel to the magnetic field, and we may take the straight arrow as indicating the direction of the magnetic field. One vibration is in the direction of this arrow. The other, circular, motions are shown by the circular arrows on the two discs. The effect discovered by Zeeman can be predicted very simply from this model, as will be shown later.

Larmor * has given a very important theorem which may be stated as follows:

Let a system of electrons describe orbits under the action of their mutual repulsions and of any other forces the directions

* Larmor, *Aether and Matter*, p. 343.

of which pass through an axis. Suppose the system subjected to the action of a uniform magnetic field $\mathbf{H}$ parallel to that axis, then the motion of the system is such that it may be represented as a possible motion for which $\mathbf{H} = 0$ combined with a precessional rotation as a whole around the axis. When the other forces are central, this applies to any direction of $\mathbf{H}$ as axis.

It may be noted that Larmor's theorem does not justify the assumption that the orbits before and after the imposition of the magnetic field are identical. It can, however, be shown from classical electro-dynamics that, to the first order in terms involving the field, the two sets of orbits are the same.*

In the case of the simplest atomic model consisting of a

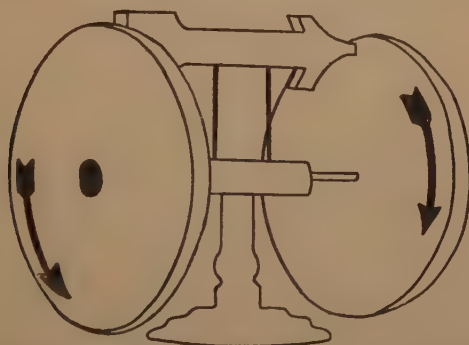


FIG. 28.—Model illustrating the Zeeman Resolution.

single electron and a massive nucleus, the angular velocity of precession is given by

$$\omega = \frac{1}{2} \frac{e}{m_0} \frac{H}{c} \quad . \quad . \quad . \quad . \quad . \quad 15:2$$

The classical value for the change in frequency of a vibrating electron, due to a magnetic field, follows at once from Larmor's theorem. The effect of the magnetic field is to superimpose an angular velocity of amount ω on the original motion of the electron. This means a change in frequency numerically equal to $\frac{\omega}{2\pi}$, so we may write

$$\begin{aligned} \Delta\nu &= \pm \frac{\omega}{2\pi} \\ &= \pm \frac{e}{m_0} \frac{H}{4\pi c} \quad . \quad . \quad . \quad . \quad . \quad 15:3 \end{aligned}$$

* W. M. Hicks, *Nature*, vol. 115, p. 978, 1925; A. M. Mosharrafa, *Nature*, vol. 116, p. 96, 1925.

If we are observing in the direction of the field, electrons moving in a clockwise direction will have their frequency increased.

We must now consider how the light waves are affected by the motion of the electrons. In the classical theory a vibrating electron gives rise to an electromagnetic wave of the same frequency as that of the vibration. First we consider the light emitted parallel to the lines of force. In practice, to show this longitudinal effect the pole pieces of the magnet would have to be bored through, so that we could observe along the lines of magnetic force. The result may easily be seen from an examination of the model. The original light splits up into two components which are circularly polarized, the polarization of one component being right-handed and the other left-handed. In accordance with our equation there will be a difference in frequency due to the magnetic field equal to $\Delta\nu$, and so we get the longitudinal effect shown in the diagram (Fig. 26).

In the next place let us consider the light which is emitted in a direction normal to the lines of force, for example, in the direction OX in our original figure. The vibrations parallel to the lines of force give rise to a plane polarized ray of the same frequency as the original ray. In the absence of the magnetic field the light which is due to the two circular motions will also be plane polarized, because the electron orbits are, as it were, seen sideways. Consequently we get plane polarized light in the two components, which are displaced by an equal amount corresponding to the signs $+$ and $-$ in the formula. We see, then, that the simple theory predicts in the transversal effect the normal triplet. It should be mentioned that the observations of the Zeeman effect enable us to determine the ratio of e to m_0 , and the first experiments gave the result that e/m_0 is of the order of magnitude 10^7 E.M.U. per gram (1896). In 1897 Zeeman found a more accurate value, 1.6×10^7 . Lohmann,* from observations on helium, obtained the value 1.737×10^7 . Weiss and Cotton,† from measurements on the blue line of zinc (wavelength 4680) found 1.767×10^7 , and Gmelin‡ very nearly the same value, 1.771×10^7 . These values, which were the first determinations of e/m_0 from optical observations, agree very closely with the results obtained in other ways. In fact, the mean value found from other observations is 1.77×10^7 E.M.U. per gram.

We may note, too, that the Zeeman effect enables us to determine the sign of the charge carried by the vibrating electron, and shows that the charge is negative.

* Lohmann, *Phys. Zeits.*, vol. 7, p. 809, 1906.

† Weiss and Cotton, *Journ. de Phys.*, vol. 6, p. 429, 1907.

‡ Gmelin, *Ann. d. Physik*, vol. 28, p. 1079, 1909.

2. The Quantum Theory of the Zeeman Effect

Difficulty is met with in applying the quantum theory even in the case of the simple Zeeman effect. The problem has been discussed by a number of workers, including Herzfeld,* Bohr, † and later Debye ‡ and Sommerfeld.§ Considerable progress has been made in the solution of the problem by the last two on this list. The difficulty of accounting for any effect at all had been emphasized by Mosharrafa,|| and more recently by Hicks,¶ the former having shown how the extended form of the quantum restrictions put forward by W. Wilson leads to the simple Zeeman effect. Wilson himself has also discussed this problem.

We shall, however, consider only the simple deduction of the Zeeman separation due to Sommerfeld. According to Bohr's second postulate radiation is emitted only in the transition between two stationary states, the frequency ν of the emitted spectral line being determined by the relation $h\nu = H_a - H_e$, where H_a and H_e are the initial and final energies of the system. The effect of the magnetic field is to produce a change in the energy in the initial state of amount ΔH_a , and in the final state of amount ΔH_e .

Consequently there is a change in the frequency of the radiation emitted determined by the equation

$$h\Delta\nu = \Delta H_a - \Delta H_e \quad . \quad . \quad . \quad 15:4$$

It is necessary then to determine the change in the energy of a stationary state due to some applied magnetic field of strength H . Sommerfeld supposes that orientation in space occurs as described in a previous chapter, but finds that there is no change in the form of the orbit, the change in energy being equal simply to the change in the kinetic energy, and the amount of this change ΔH is equal to $m \frac{h}{2\pi} \mathbf{o}$ where $\mathbf{o}$ is the angular velocity corresponding to the Larmor precession. When we substitute the value for $\mathbf{o}$ we obtain

$$\Delta H = m\hbar \frac{e}{m_0} \frac{H}{4\pi c} \quad . \quad . \quad . \quad 15:5$$

In this expression m is the equatorial or magnetic quantum number which determines the resolved angular momentum about the

* Herzfeld, *Phys. Zeits.*, vol. 15, p. 193, 1914.

† Bohr, *Phil. Mag.*, vol. 27, p. 506, 1914.

‡ Debye, *Phys. Zeits.*, vol. 17, p. 507, 1916.

§ Sommerfeld, *Phys. Zeits.*, vol. 17, p. 491, 1916.

|| Mosharrafa, *Proc. Roy. Soc. A*, vol. 102, p. 529, 1923.

¶ Hicks, *Nature*, vol. 115, p. 978, 1925.

direction of the field. Introducing an expression of this form for ΔH_a and ΔH_e , the equation becomes

$$h\Delta\nu = (m_a - m_e) \times h \frac{e}{m_0} \frac{H}{4\pi c} . . . 15:6$$

We notice that h , the quantum constant, occurs on both sides of the equation, and cancels out, leaving us with

$$\Delta\nu = (m_a - m_e) \frac{e}{m_0} \frac{H}{4\pi c} . . . 15:7$$

As Sommerfeld remarks—"In our final formula the quantum theory has, in a certain sense, become latent, in that its characteristic feature, the quantity h , has disappeared." In this we see a reason for the possibility of accounting for the Zeeman effect on the classical theory.

The change in frequency depends on the difference between the two quantum numbers m_a and m_e . In ordinary cases a "selection principle" is introduced limiting the change in the equatorial quantum number to the values ± 1 or 0. In the first case, when the difference between these numbers is ± 1 , the frequencies of the resulting components are given by

$$\nu = \nu_0 \pm \frac{e}{m_0} \frac{H}{4\pi c},$$

and each of these lines is circularly polarized in a plane perpendicular to the field. When viewed longitudinally these lines appear circularly polarized, and when viewed transversely they appear plane polarized, perpendicular to the lines of the field. In the second case, when $m_a - m_e = 0$, i.e. when the equatorial quantum number is unchanged, the line only appears when viewed transversely, for it is plane polarized with its electric vector parallel to the direction of the field.

Thus the normal triplet can be accounted for by applying the quantum theory.

3. Anomalous Zeeman Effects

In actual observations normal Zeeman resolution is the exception rather than the rule. It is convenient to consider the change *in a term* due to an applied magnetic field. We may regard the change ΔH in the energy of a term as being equivalent to a certain change in frequency represented by $\Delta\nu$ where

$$\begin{aligned} h\Delta\nu &= \Delta H \\ &= m \frac{he}{m_0} \frac{H}{4\pi c} \\ \Delta\nu &= m \frac{e}{m_0} \frac{H}{4\pi c} \\ &= m\Delta\nu_n 15:8 \end{aligned}$$

where $\Delta\nu_n$ stands for $\frac{e}{m_0} \frac{H}{4\pi c}$, and may be termed the normal change. Thus the frequency change for a term should be an integral number of times the classical value $\Delta\nu_n$. In the anomalous separation this relation does not hold.

It has been found convenient to generalize this expression for the term displacement by introducing a numerical factor g , and writing

$$\Delta\nu = mg\Delta\nu_n \quad . \quad . \quad . \quad . \quad . \quad 15:9$$

This quantity g has been termed the Landé "splitting factor." The empirical observations can be represented by assuming that for each term g has a characteristic value which may be expressed as a rational fraction.

In the study of the observations of the Zeeman effect two important generalizations have been made.

(1) *Preston's Rule* (1899).—In a magnetic field all the lines belonging to the same series of an element undergo the same resolution on the scale of frequency. Also corresponding lines of different elements behave in the same way.

This means that lines which are composed of similar terms give rise to the same Zeeman effect, and implies that the Zeeman type is independent of the radial quantum number.

(2) *Runge's Rule* (1907).—In the anomalous Zeeman effect the separation of the components from the zero position (expressed as a frequency) is a small multiple of an aliquot part of the normal Lorentz resolution. The equation containing g is the mathematical expression of this rule. The rule may be illustrated for the D-lines of sodium. In the magnetic field the line D_1 splits up into four components which we may describe as the parallel and the perpendicular components, the line D_2 splits up into six components.

$$D_1 \left\{ \begin{array}{l} \Delta\nu = \pm \frac{2}{3} \Delta\nu_n \\ \Delta\nu = \pm \frac{1}{3} \Delta\nu_n \end{array} \right. \quad D_2 \left\{ \begin{array}{l} \parallel \Delta\nu = \pm \frac{1}{2} \Delta\nu_n \\ \perp \Delta\nu = \pm \frac{3}{2} \Delta\nu_n \\ \text{or } \Delta\nu = \pm \frac{5}{2} \Delta\nu_n \end{array} \right.$$

In applying Runge's rule it should be remembered that the *terms* are of greater theoretical importance than the *lines*.

Paschen and Back* made the important discovery that the type of resolution depends on the strength of the magnetic field. In a field that is "strong" relatively to the line considered, every line configuration behaves like a simple line, and exhibits the normal Zeeman effect (Sommerfeld, pp. 388–9).

Many exceptions to Preston's rule may be explained by taking into account this Paschen-Back effect.

* Paschen and Back, *Ann. d. Physik*, vol. 39, p. 897, 1912.

4. Multiplicity of Spectral Terms

The four chief spectral series may be written (p. 51)

$$\begin{aligned} P(m) &= 1S - mP \\ S(m) &= 1P - mS \\ D(m) &= 1P - mD \\ F(m) &= 2D - mF \end{aligned}$$

Here $D(2)$, for example, indicates the *line* in the Diffuse or D series for which $m = 2$, while $2D$ is equivalent to the *term* $N/(2 + D)^2$.

These formulæ represent the four chief series of a "singlet" system, but in many cases spectral lines occur as doublets (as in the case of the D-lines of sodium), triplets, etc.; thus the terms from which the spectral lines are derived are two-fold, three-fold, etc. In forming the possible combinations we must take into account this "multiplicity" of the terms, though it must be observed that some of the components which are possible algebraically are inadmissible physically. The S term is always simple (one-fold), whereas the P term, D term and the F term have larger multiplicity and may be two-fold, three-fold, etc. This similarity of subdivision which is found for the various terms is called the *permanency of the multiplicities*. The problem of accounting for these multiplicities stands in intimate relationship to the problem of the anomalous Zeeman effect. In both cases the existence of an intra-atomic magnetic field has been postulated to account for the observed results. This explanation is in harmony with the fact that multiplicity and valency vary together: we find doublets in the case of uneven valency, and triplets in the case of odd valency. As valency is associated with the number of outer electrons of the atom, the origin of the inner magnetic field appears to be related to the number of those outer electrons. By work on these lines Landé* and also Sommerfeld† have been able to co-ordinate the phenomena connected with the multiplet structure of spectral terms and the general Zeeman effect. Mention must also be made of the suggestive work of Heisenberg.‡

It would appear then that doublet separations, such as are observed in the spectra of the alkali elements, are manifestations of what is practically a Zeeman effect produced by an internal atomic magnetic field. To account for the observed separations, the fields, for some atoms at least, must be exceedingly high (of the order 10^6 or 10^7 gauss). When the external field is great as compared with the internal, theory shows that for doublets

* Landé, *Zeits. f. Physik*, vol. 15, p. 189; vol. 19, p. 122, 1923.

† Sommerfeld, *Ann. d. Physik*, vol. 73, p. 209, 1924.

‡ Heisenberg, *Zeits. f. Physik*, vol. 8, pp. 257, 273, 1922.

and triplets the final result is a normal Zeeman triplet, in accord with the experimental observations of Paschen and Back.

To correlate the experimental results as regards multiplicities it is necessary to introduce the quantum number j , the "inner quantum number." Thus a spectral term is, as we have seen, associated with a total quantum number n , an azimuthal number k , and an inner quantum number j . For S, P, D . . . terms, k has the values 1, 2, 3 . . . and normally only those transitions occur for which k changes by unity. According to "the selection principle for inner quantum numbers" the only transitions possible are determined by

$$j \rightarrow j \mp 1, j \rightarrow j.$$

Thus, in this case, the transition $\Delta j = 0$ is not forbidden.

Sommerfeld has assigned values for j corresponding to the S, P, D terms, and to various values of the multiplicity r . In his scheme j is integral for odd multiplets, but for even multiplets is an integer plus one-half. "In a magnetic field each nkj term splits up into $2j + 1$ equidistant components; and the separation of these from the original position expressed in wave numbers is given by

$$\Delta\nu = mg\Delta\nu_n \quad \dots \quad 15:9$$

Here $\Delta\nu_n$ is the normal Larmor separation ($eH/4\pi m_0 c$), m the magnetic quantum number which takes the values $j, j - 1, j - 2, j - 3 \dots -j$ for each j term (and hence is integral for odd multiplets, and half-integral for even multiplets), and g the Landé 'splitting factor' which may be written as

$$g = \frac{3}{2} + \frac{\left\{\frac{r}{2} - (k - \frac{1}{2})\right\} \left\{\frac{r}{2} + (k - \frac{1}{2})\right\}}{2j(j + 1)}. \quad 15:10$$

The expression then covers completely the observations on the Zeeman effect in a weak magnetic field for ordinary spectra."

We see, then, that the splitting factor of Landé is an empirical number which determines the change in the frequency of a term due to a magnetic field. If we substitute Sommerfeld's values (pp. 65-6) for r and k , viz. $\frac{r}{2} = s + \frac{1}{2}$, $k = l + 1$, in the above equation, we find

$$g = \frac{3}{2} + \frac{\{(s + \frac{1}{2}) - (l + \frac{1}{2})\} \{(s + \frac{1}{2}) + (l + \frac{1}{2})\}}{2j(j + 1)},$$

which reduces to

$$g = 1 + \frac{j(j + 1) + s(s + 1) - l(l + 1)}{2j(j + 1)}. \quad 15:11$$

Many attempts were made before 1926 to give a physical interpretation to this formula, and for these reference may be made to Stoner's book, *Magnetism and Atomic Structure* (pp. 237-8). It was possible to obtain on theoretical grounds an expression of the form:

$$g = 1 + \frac{J^2 + J_s^2 - J_a^2}{2J^2} \quad . \quad . \quad . \quad 15:12$$

This formula bears considerable resemblance to the empirical formula, but if we adopt the older quantum theories we cannot get exact agreement. The newer quantum theories associated with the names of Heisenberg and Schrödinger introduce modifications which are equivalent to writing J^2 in the form $j(j+1)$.

In order to obtain this formula it was necessary to assume that the contribution of the core to the magnetic moment of the atom is twice as great as would be expected from its angular momentum. As we shall see in the next chapter, the hypothesis of the spinning electron removes this difficulty.

Stoner concluded that electron orbits and cores are characterized by integral magnetic moments (in terms of the Bohr unit). The magnetic moment of an electron orbit is assumed to be given by the azimuthal quantum number k . The maximum magnetic moment of the cores was then found equal to the number of electrons it contains in uncompleted groups, i.e. to the number of "outer" electrons in the core, if we define "outer" electrons as those the core possesses in addition to those forming a completed configuration. The maximum term multiplicity is greater by two than the magnetic moment of the core, μ_c , that is $\tau = \mu_c + 2$. Magnetic balancing in pairs of core electrons gives rise to lower multiplicities, all odd or all even for odd or even numbers of core electrons.

Intensities of the Components.—Much important work on the intensities of multiplet lines has been done at Utrecht by Professor Ornstein and his fellow-workers Burger and Dorgelo. By means of certain "summation rules" which have been put forward, it is possible to obtain results which agree closely with the experimental determinations. Employing the inner quantum numbers of Sommerfeld, each n, k, j term splits up in a magnetic field into $2j+1$ equidistant components. Then P , which is equal to $2j+1$, determines the number of possible and equally probable ways in which the nkj state can be realized, and is consequently called the statistical weight of the term. The "summations rules" provide a relation between the *sum* of the intensities of the line components produced by certain transitions and the corresponding statistical weights.

5. Magnetic or Relativity Doublets

Observations on the anomalous Zeeman effect lead to the conclusion that optical doublets must have a magnetic origin. It seems justifiable to apply the same reasoning to the case of X-rays, although for X-rays Sommerfeld has interpreted terms such as L_{II} and L_{III} as simple relativity doublets and has shown that their separations can be calculated accurately on that basis. Landé* has pointed out that the relativity and optical doublet separations can both be represented by the same general formula. The view that the optical and X-ray doublets are essentially similar in origin is borne out by the distribution of electrons in various levels advocated by Stoner.

Sommerfeld draws the following important conclusion from Larmor's theorem :

"The electron describes in the magnetic field the same path as when no magnetic field is acting but doing so with respect to a system of reference which is rotated with the velocity $\mathbf{o}$. Regarded from the standpoint of this system of reference the orbits are traversed as if no field were present. Precession of the system of reference and action of the magnetic field are interchangeable and equivalent to one another."

In view of this statement we may reverse the order and consider precession (as it occurs for instance in relativity theory) as replaced by the action of a magnetic field. From a mathematical standpoint it may be simpler to replace a magnetic field by a motion of precession. From a physical standpoint it may be simpler to replace a motion of precession by the action of a magnetic field. These remarks are of importance in connection with the work of Millikan and Bowen† on "stripped" atoms, i.e. atoms which have been stripped of practically all their electrons. These authors conclude that their results require one of two alternatives: (1) discarding the relativity explanation of X-ray and optical doublets and with it all relativity effects in electronic orbits, or (2) introducing a dissymmetry not heretofore contemplated in atomic models, abandoning Bohr's interpenetration ideas and his assignment of azimuthal quantum numbers.

Here, then, the older quantum theories led to conflicting results. There appeared to be two different types of explanation, one in terms of relativity, the other in terms of a magnetic field. By the employment of the spinning electron it is possible to account for all the results in terms of a single theory.

* Landé, *Zeits. f. Physik*, vol. 24, p. 88, and vol. 25, p. 46, 1924.

† Millikan and Bowen, *Phys. Rev.*, vol. 24, pp. 209, 223, 1924.

CHAPTER XVI

SPINNING ELECTRONS

Without any assertion of finality in the description of electronic interactions by its means, the importance of the spinning model of the electron can scarcely be overestimated. Yet the spinning electron has been so lost in the far wider ideas embodied in the new mechanics that it is as yet scarcely appreciated at its full value. . . .

The spinning electron has brought order out of chaos in the broad outlines of atomic theory. Its necessity and its successes are qualitatively independent of the new mechanics.

R. H. FOWLER, *Nature*, January 15, 1927

1. Early Work on Spinning Electrons

THE conception of a rotating electron has been suggested by many investigators. Reference may be made to the work of Voigt (1902), and of Abraham (1903), and it is of interest to notice that Ritz in his magnetic model of 1908, in which he attempted an interpretation of spectral series, definitely put forward the idea that his elementary magnets might be composed of electrically charged bodies rotating about an axis. McLaren in 1913 described a magneton which was endowed with an angular momentum of amount $h/2\pi$. It is true that in one sense this magneton cannot be described as a spinning electron, for McLaren rejected entirely the idea of electric or of magnetic substance, and supposed that the angular momentum of the magneton was to be found in the electro-magnetic field. The essential fact remains that McLaren first postulated a physical unit endowed with the quantum of angular momentum.

In a discussion on the structure of the atom at the Royal Society on March 19, 1914, in referring to the magnetic moment of the magneton, the author* made a tentative suggestion that the core of an atom might be regarded as a revolving sphere of positive electricity, or, alternatively, that the electron might be a revolving sphere of negative electricity.

Another type of spinning electron is the magneton or "anchoring" electron of A. L. Parson (1915) in which a ring of negative

* H. S. Allen, *Nature*, vol. 92, p. 713, 1914; *Phil. Mag.*, vol. 29, p. 714, 1915.

electricity spins about its axis with high velocity. The author* has pointed out the capacity of this model for explaining optical activity and optical isomerism, and has made estimates of the constants of the ring electron, assuming that the angular momentum is determined by the usual quantum condition. The local magnetic field quite near the ring assumes a very high value, being of the order 10^8 gauss at a distance equal to the diameter of the ring.

In a paper read before the American Association for the Advancement of Science in December, 1920, A. H. Compton† concluded that the electron itself, spinning like a tiny gyroscope, is probably the ultimate magnetic particle. Reference was made to the ring electron and also to Nicholson's idea of an electron with a strong concentration of electric charge near the centre, and a quantized spin was suggested for the electron which may perhaps be regarded as a sphere.

Apart from a disinclination to attribute any structure to the electron, perhaps the chief objection to these early models was due to the fact that the size of the electron seemed too large to be in harmony with prevailing theories. The size was determined by assuming the peripheral velocity to be not greater than the velocity of light.

2. The Spinning Electron and the Bohr Atom

Two Dutch physicists, Uhlenbeck and Goudsmit,‡ in interesting letters published at the end of 1925 and the beginning of 1926, ignored the difficulties arising from velocities in excess of the velocity of light, and boldly applied the hypothesis of the spinning electron to the motion of an electron round a nucleus. They considered the effect which would be produced by the quantized spin of the electron on the manifold of the stationary states.

According to Eddington§ the theory of relativity raises no objection to the periphery of the spinning electron moving faster than light. "It is only when *energy* or *signals* are alleged to go faster than light the relativity theory is moved to intervene." The mass and energy of an electron are considered as residing in the electro-magnetic field, outside its boundary. "In describing the electron as spinning . . . we make our thought skip faster than light round its boundary and by so doing succeed in seeing

* H. S. Allen, *Phil. Mag.*, vol. 40, p. 426, 1920; vol. 41, p. 113, 1921.

† A. H. Compton, *Journ. Frank. Inst.*, p. 145, August, 1921.

‡ Uhlenbeck and Goudsmit, *Naturw.*, vol. 13, p. 953, 1925, and *Nature*, vol. 117, p. 264, 1926; *Zeits. f. Physik*, vol. 35, p. 618, 1926.

§ Eddington, *Nature*, vol. 117, p. 652, 1926.

a correlation with a more familiar structure, viz., that of an electron at rest. The correlating velocity has no more physical existence than has the factor $\sqrt{-1}$ used to correlate the structure of the four-dimensional world to the more familiar structure of a four-dimensional Euclidian space."

Independently, a tentative suggestion that the electron is a charged magnetic doublet was made in America by Bichowsky and Urey.* They claimed that on their hypothesis it seemed possible to explain relativity doublets and also anomalous Zeeman effects.

The way in which this magnetic electron influences stationary states is not difficult to understand. Since the electron possesses a magnetic moment and is moving in the electric field of the nucleus, it will be acted on by a couple, and this couple will cause a slow precession of the spin axis. To ensure the conservation of the angular momentum of the atom there would be a compensating precession of the orbital plane of the electron. Corresponding to each stationary state of a Bohr atom in which the electron has no spin, there will, in general, be a set of states which differ in the orientation of the spin axis relative to the orbital plane. For a one-quantum spin there will be in general two such states. Further, it can be shown that the energy difference of these states will be proportional to the fourth power of the nuclear charge.

For the interpretation of complicated spectra it is necessary to assign to every electron *two* quantum numbers. The first of these must correspond to the azimuthal quantum number which determines the moment of momentum of the electron about the nucleus. According to Uhlenbeck and Goudsmit the second quantum number may be regarded as specifying the moment of momentum of the electron itself. This may be illustrated by some applications to the finer structure of spectra.

(1) Sommerfeld's explanation of the fine structure of hydrogen-like spectra is now modified, and the Dutch authors consider as an illustration the energy levels corresponding to electronic orbits for which the principal quantum number is equal to three. In the diagram (Fig. 29) are given on the left the results to be expected from the older theory, the levels being fixed by the azimuthal quantum number k (where $k = 1, 2, 3$), and on the right the levels given by the new theory.

The moment of momentum of the electron about the nucleus is now given by $Kh/2\pi$, where $K = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$. The total angular momentum of the atom is $Jh/2\pi$ where $J = 1, 2, 3$. In the absence of electron spin the dotted lines show the position of the

* Bichowsky and Urey, *Nat. Acad. Sci. Proc.*, vol. 12, p. 80, February, 1926.

energy levels, but, as the arrows indicate, this spin splits each level into two, with the exception of the level $K = \frac{1}{2}$, which is only displaced.

The symbols K and J used in Fig. 29 correspond to those used by Landé, but are somewhat old-fashioned. We should now replace K by l of the new mechanics, and J by j , the new quantum numbers being $\frac{1}{2}$ less than the old.

Born has emphasized the fact that many of the difficulties

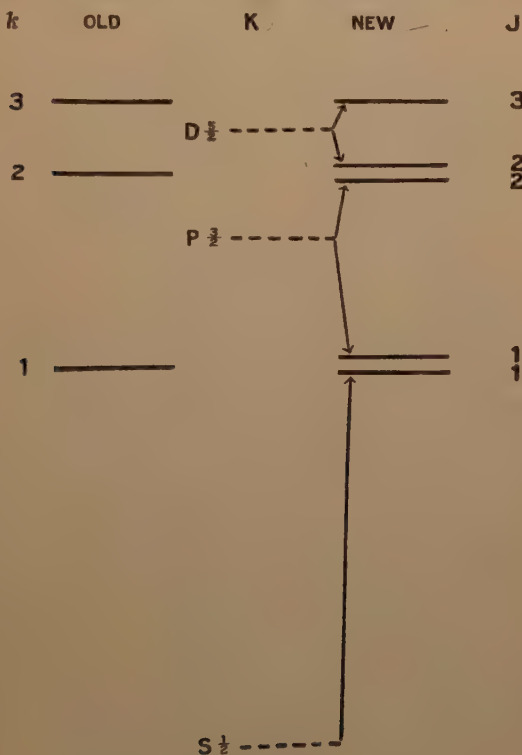


FIG. 29.—Energy Levels.

in explaining the existence of multiplets in spectra and the observations of the anomalous Zeeman effect have arisen from the use of an incorrect model, in which the electron was treated as a charged mass-point. If we assume with Uhlenbeck and Goudsmit* that the electron possesses angular momentum and a magnetic moment these difficulties may be removed.

(2) *Multiplets*.—There is a remarkable analogy between the multiplet structure of optical spectra and the structure of X-ray

* Goudsmit and Uhlenbeck, *Zeits. f. Physik*, vol. 35, p. 618, 1926.

spectra. This analogy, which has been the subject of much discussion, is difficult to explain satisfactorily on the basis of a relativity effect. If, however, we adopt the hypothesis of the spinning electron, an immediate explanation is obtained.

The well-known doublets in spectra of the alkaline type, of which the D-lines of sodium form a conspicuous example, are now to be regarded as regular spin-doublets. This view enables us to explain the dependence of the doublet separation on the effective nuclear charge and the quantum numbers describing the orbit, as well as the rules of combination.

In the atom of an alkali a single electron describes an orbit round an atomic residue containing only completed electronic groups, which are magnetically inert. But as the electron has a magnetic moment, its axis will experience a precession because of the couple due to its motion in the electric field. There will also be a corresponding secular perturbation of the plane of the orbit. It can then be shown that the energy of a single orbit splits up into a set of energies, the differences between which vary as Z^4 as required by the observations. L. H. Thomas has obtained a separation formula giving correct numerical values.

When we pass to atoms in which several atoms revolve round a magnetically inert core, the results are more complicated as there are other directing influences on the axis of each spinning electron. Multiplets of higher complexity now make their appearance, and although it may be difficult to give a quantitative explanation of the phenomena observed, we can account for them in a general way by means of the new hypothesis.

(3) *The Zeeman Effect*.—The introduction of the spinning electron was primarily suggested by the anomalous Zeeman effect. The simple Lorentz resolution demanded by Larmor's theorem is found only for lines of singlet systems. In practice the components of multiplet structures show anomalous effects which formerly gave rise to grave difficulties in the attempt to explain them. The more complicated structures usually observed can be described by introducing a "splitting factor." This anomaly could be explained formally if the magnetic moment of the atom arose from two sources, one of these being the orbital angular momentum. According to Uhlenbeck and Goudsmit the difficulties disappear at once when it is assumed that the electron has a spin, for the spinning electron provides a second source of magnetic moment, and it has been shown that a qualitative explanation can then be given.

On the basis of the restricted theory of relativity the kinematics of an electron with an axis has been discussed by Thomas.*

* L. H. Thomas, *Nature*, vol. 117, p. 514, 1926; *Phil. Mag.*, vol. 3, p. 1, 1927.

The result obtained has great physical interest for it shows that the assumptions of Uhlenbeck and Goudsmit really lead to the correct doublet separation and at the same time to an explanation of the anomalous Zeeman effect, when the problem is treated by the new quantum mechanics. Thus the theory of the spinning electron connects the anomalous Zeeman effect with the optical and relativity doublets, and accounts for them as manifestations of the magnetic properties of the electron. It must be supposed that the axis of the electron precesses about a magnetic field with an angular velocity differing from that of the Larmor rotation. In fact an angular velocity $(e/m_0c) \mathbf{H}$, twice the Larmor precession, must be assumed. Starting from this idea, values of the Landé factor, g , can be obtained differing from unity. The procedure may be outlined as follows: Assuming that the electron has the above-mentioned precession about the magnetic field in a system of axes in which its centre is instantaneously at rest, the secular rate of change of direction of its axis when it revolves in an orbit can be found. "Assuming that there is some total angular momentum which is secularly conserved, that which the electron itself adds to that of the orbit having magnitude $\hbar/4\pi$, the secular motion of the system can be found. An approximate formula for the doublet and Zeeman effect separations follows. The new quantum mechanics of Heisenberg transforms this into a formula which fits the observed doublet separations and Zeeman effect exactly, as far as first order terms in the relativity correlation are sufficient."

(4) *Paschen-Back Effect*.—The gradual transformation of the multiplet structure as the magnetic field increases, known as the Paschen-Back effect (p. 211), can be explained by supposing that the influence of the field on the precession of the spin axis becomes comparable with the effect due to the orbital motion in the atom.

(5) *Statistical Weight*.—Another paradox which has been resolved by means of this spinning electron is that in connection with the statistical weight of a term. By this we mean the total number of states which must be associated with a particular spectral term. The weight to be assigned to the core is R , where R denotes the maximum multiplicity. If the electron be a point charge the total number of states of total quantum number n must be asymptotically equal to n^2 for large values of n , and the total number of states of core and orbital electron must be R_n^2 . Actually it is found to be $2R_n^2$ for all values of n in all cases. The only way out of this difficulty is to suppose that the electron has a structure.

(6) *Atomic Models*.—The capabilities of the spinning electron in the construction of models of atoms and also of molecules

have not as yet been fully investigated, but it must be remembered that these were implicit in the magneton of A. L. Parson and were taken for granted in the static models of Lewis and Langmuir. It need only be said here that the difficulties of explaining the diamagnetic properties of hydrogen and helium when the Bohr model is employed, disappear on the introduction of electrons which possess magnetic moment.

The remarkable results obtained by employing the spinning electron in Bohr's atomic model suggest the idea that the proton also may be capable of a quantized spin. If, as is generally assumed, the proton is the positive electron, it seems natural to assume that if the negative electron can spin with unit angular momentum the positive may do the same. Again, it may be easier to understand the structure of a complex nucleus if the units of which it is composed can act as elementary magnets. Duane * has attempted to explain corpuscular emission from a radioactive nucleus on these lines. According to O. W. Richardson,† it is probable that the electron loses its angular momentum when it enters into the nucleus, but the magnitude of the mechanical gyromagnetic anomaly makes it necessary to admit the existence of a quantized spin of the nucleus as a whole. Finally experiments on the deflection of protons and alpha particles in collision with an atomic nucleus lend support to the idea that a magnetic field exists in the vicinity of a nucleus.

3. The Gyromagnetic Electron of L. V. King

A rotating spherical charge sets up a magnetic field, which was investigated by Maxwell in 1870. The internal field is uniform and of strength $\frac{2}{3}e\omega/a$, while the external field is that of a magnetic doublet of moment $\frac{1}{3}e\omega a^2$, where ω is the angular velocity and a the radius of the sphere.

A simple type of spinning electron based on Maxwell's work has been discussed by L. V. King,‡ who has attempted to give a theory of atomic structure and radiation by using classical electrodynamics. His work is of great interest, and although it obviously cannot claim finality, the attempt shows that the resources of classical theory have by no means been exhausted. When the spinning electron is moving in a specified direction with velocity v , it is deformed by translation into an ellipsoid, the short axis being in the direction of motion. Regarding this as a real, physical deformation, the total energy of the field due both to translation and to spin, including the work done by the boundary stresses (probably magnetic in origin) is similar in form

* Duane, *Phys. Rev.*, vol. 5, p. 335, 1915.

† Richardson, *Nature*, vol. 117, p. 652, 1926.

‡ L. V. King, *Gyromagnetic Electrons* (Louis Carrier, Montreal, 1926).

to that of a rigid body. The final result found gives the energy as

$$T = mc^2 + \frac{1}{2}(A\omega_1^2 + B\omega_2^2 + C\omega_3^2) + \text{constant} \quad 16:1$$

In the first term $m = m_0/(1 - \beta^2)^{1/2}$ where $m_0 = \frac{2}{3}e^2/a$ and $\beta = v/c$. The components of spin are $\omega_1, \omega_2, \omega_3$, and the electrodynamic moments of inertia may, in general, be expressed in the form

$$A = I(1 + a_1\beta^2 + a_2\beta^4 + \dots), \quad B = C = I(1 + c_1\beta^2 + c_2\beta^4 + \dots),$$

where $I = \frac{1}{2}m_0a^2$ is the moment of inertia of the spinning electron at rest.

It appears probable that the boundary conditions adjust themselves so that the interior fields of the electron remain unchanged at the velocity under consideration. This assumption leads to the classical expressions for the force on an electron in an electric or magnetic field.

The spinning or gyrostatic electron moving with uniform velocity under no forces has a single precessional frequency ν given by

$$2\pi\nu = \Omega_1(C - A)/C = \Omega_1(c_1 - a_1)\beta^2(1 + b_1\beta^2 + b_2\beta^4 + \dots) \quad 16:2$$

where Ω_1 is the constant intrinsic spin of the electron.

Fitzgerald has shown that an oscillating magnet can radiate electromagnetic waves, so that ν may be regarded as the frequency of the emitted radiation.

If we put

$$h\Omega_1 = \pi c^2 m_0 / (c_1 - a_1) \quad \dots \quad 16:3$$

where $(c_1 - a_1)$ is a numerical constant equal to $2/5$ for the simple model considered, we find to a first approximation:

$$h\nu = \frac{1}{2}m_0v^2 \quad \dots \quad 16:4$$

the well-known photo-electric equation.

Planck's constant then appears as a quantity characteristic of the spinning electron, and dependent on its intrinsic spin.

It is claimed that with similar hypotheses as to spinning protons the series formula for line spectra can be deduced, and the correct value for the Rydberg constant obtained. The photo-electric equation used in conjunction with a Maxwellian distribution of electron velocities, also leads, with reasonable hypotheses as to electron orbits in a space lattice, to Planck's formula for black-body radiation and the associated formulæ for specific heats.

Although objections may be raised against certain features of the exposition, the attempt is interesting as indicating that there are still possibilities in the construction of models which in certain respects conform to the classical laws. There remains the difficulty of accounting for an intrinsic spin which is to be the same for all electrons.

CHAPTER XVII

THE NEW QUANTUM MECHANICS

It is to be hoped that a new era of mutual stimulation of mechanics and mathematics has commenced. To the physicists it will at first seem deplorable that in atomic problems we have apparently met with such a limitation of our usual means of visualization. This regret will, however, have to give way to thankfulness that mathematics, in this field too, presents us with the tools to prepare the way for further progress.

NIELS BOHR, *Nature*, December 5, 1925

1. The Work of Heisenberg

IN the nineteenth century classical electrodynamic theory had considerable success in explaining many of the phenomena of atomic physics, but other facts emerged which seemed to necessitate a radical departure from this theory. During the first quarter of the present century many attempts were made to meet these difficulties by means of special assumptions and rules, which constituted the quantum theory. Although these methods have had remarkable success in the interpretation of a restricted set of phenomena, it has long been felt that such a procedure, designedly adopted with a particular end in view, was not satisfactory and that a more general theory was required.

In 1925 Heisenberg * put forward a new theory of quantum mechanics which has had far-reaching consequences, and seems to point the way to a complete solution of the problem from the mathematical standpoint. One of the fundamental ideas employed by Heisenberg is that only such things as are directly open to observation should enter into the mathematical formulation. He considered it advantageous to avoid every concept which cannot be connected with experiment, and so eliminated all ideas of motion within the atom. We are unable to assign to an electron a special position in space at a special instant of time, so that, *as far as our observations are concerned*, an electron orbit does not exist. In attempting to build up a new quantum mechanics in which relations between observable magnitudes

* Heisenberg, *Zeits. f. Physik*, vol. 33, p. 879, 1925.

alone should enter, Heisenberg took as his starting point the frequency relation of Kramers' dispersion theory.

The chief problem to be solved by the quantum theory consists in determining the frequencies and amplitudes of the emitted radiation and the energy levels of the atomic system. It is known that the frequencies of spectral lines can be expressed according to the quantum theory in the form :

$$\nu(n, n - a) = \frac{1}{h} \{W(n) - W(n - a)\} \quad . \quad . \quad 17:1$$

where the expression $\nu(n, n - a)$ implies that the frequency is a function of the two quantum numbers, n and $n - a$.

In the classical theory the corresponding expression may be written

$$\nu(n, a) = a \cdot \nu(n) = a \frac{1}{h} \frac{dW}{dn} \quad . \quad . \quad 17:2$$

The fact that we have a certain *difference* in the first formulation and a *differential* in the second is of special significance, and suggests that the same modification of classical results may be necessary in other instances.

Again, classical frequencies conform to the combination relation

$$\nu(n, a) + \nu(n, \beta) = \nu(n, a + \beta) \quad . \quad . \quad 17:3$$

while on the quantum theory the relation is assumed as

$$\nu(n, n - a) + \nu(n - a, n - a - \beta) = \nu(n, n - a - \beta) \quad 17:4$$

In addition to the frequencies it is necessary for the description of the radiation to know the amplitudes.

The amplitudes may be denoted by complex three-dimensional vectors A , which define intensity, polarization and phase. Heisenberg considers some assigned quantity $x(t)$ represented by the *totality* of terms $A(n, n - a)e^{i\omega(n, n - a)t}$, this form being suggested by the expression for the co-ordinates of any particle in a classical multiply-periodic system.* In the new theory he writes :

$$x(t) = \sum_{-\infty}^{\infty} A(n, n - a)e^{i\omega(n, n - a)t} \quad . \quad . \quad 17:5$$

and proceeds to inquire what will be the value of $x^2(t)$. On the quantum theory he considers the simplest and most natural assumption to be

$$x^2(t) = \sum_{\beta = -\infty}^{\beta = +\infty} B(n, n - \beta)e^{i\omega(n, n - \beta)t} \quad . \quad . \quad 17:6$$

* For a clear account of such systems see J. H. van Vleck, *Quantum Principles and Line Spectra* (1926).

$$\text{where } B(n, n - \beta) = \sum_{\alpha = -\infty}^{+\infty} A(n, n - \alpha) A(n - \alpha, n - \beta).$$

This suggests that the product of two quantities $x(t)$ and $y(t)$, where $x(t)$ has the value given above and

$$y(t) = \sum_{-\infty}^{\infty} B(n, n - \beta) e^{i\omega(n, n - \beta)t}$$

is to be represented as

$$x(t) \cdot y(t) = \sum_{-\infty}^{\infty} C(n, n - \gamma) e^{i\omega(n, n - \gamma)t} \quad . \quad . \quad 17:7$$

where $C(n, n - \gamma) = \sum A(n, n - \alpha) B(n - \alpha, n - \gamma)$.

The significant feature here is that the product $x(t) \cdot y(t)$ is not the same as the product $y(t) \cdot x(t)$, so that in this rule of multiplication *the commutative law does not apply*. Shortly after Heisenberg's paper had been published it was pointed out by Born and Jordan* that the operations employed were none other than those in the algebra of matrices, and a new formulation of the quantum theory was suggested in terms of matrices.

To return to Heisenberg's work, the method of procedure may be briefly indicated. When solving a problem in the old theory an equation of motion of the form

$$\ddot{x} + f(x) = 0 \quad . \quad . \quad . \quad 17:8$$

must be integrated, and the constants in the case of periodic motion determined by means of the quantum condition

$$\oint p dq = nh \quad . \quad . \quad . \quad 17:9$$

In the new theory $x(t)$ is assumed to have the value previously indicated, this is substituted in the equation of motion and the unknown quantities determined, making use of a relation (derived in connection with dispersion theory) of the form:

$$h = 4\pi m \sum_{\alpha = 0}^{+\infty} \{ |A(n, n + \alpha)|^2 \omega(n, n + \alpha) - |A(n, n - \alpha)|^2 \omega(n, n - \alpha) \} \quad 17:10$$

As one example of the new method Heisenberg considers the "rotator" in which an electron circles round a nucleus at a constant distance a . The expression for the energy is found to be

$$W = \frac{h^2}{8\pi^2 m a^2} (n^2 + n + \frac{1}{2}) \quad . \quad . \quad 17:11$$

* Born and Jordan, *Zeits. f. Physik*, vol. 34, p. 858, 1925.

2. Matrix Mechanics

It is possible here to indicate only in broad outline the methods of the matrix mechanics due to Heisenberg, Born and Jordan. For further details the reader may be referred to a convenient summary in the German edition of Born's Massachusetts lectures, *Probleme der Atomdynamik*, 1926. R. H. Fowler* has given a shorter account in an address to the London Mathematical Society.

In the theory as developed by Born and Jordan the continuous variables of the classical theory are replaced by systems of discrete quantities (matrices †) which can be expressed by means of algebraic equations.

The theory of matrices is founded on the work of Cayley, Sylvester and H. J. Smith, and the fundamental notion is by no means difficult to grasp. Cayley considered a square arrangement of numbers as constituting a matrix. Thus nine numbers put in square formation, three by three, are called a matrix of order three, e.g.

$$A = \begin{bmatrix} 1, & 2, & 3 \\ 4, & 5, & 6 \\ 7, & 8, & 9 \end{bmatrix}, \quad B = \begin{bmatrix} 1, & 4, & 7 \\ 2, & 5, & 8 \\ 3, & 6, & 9 \end{bmatrix}$$

We may also deal with a rectangular matrix of mn numbers, arranged in m rows and n columns.

The matrix is to be thought of as a *compound* unit, an assemblage of numbers arranged in order but constituting a single entity. A simple geometrical illustration is afforded by taking $[x, y]$ as specifying in Cartesian co-ordinates the position of a point in a plane. Unless $x = y$ the point $[x, y]$ is not the same as the point $[y, x]$. "This is hint enough that, regarded as algebraic elements, we may with advantage study the behaviour of matrices, always treating them as single integral things, and not as elaborate clusters of component parts."

The determinant of a matrix must be distinguished from the matrix itself, just as the area of a triangle must be distinguished from the triangle itself. The determinants of the matrices given above are

$$|A| = \begin{vmatrix} 1, & 2, & 3 \\ 4, & 5, & 6 \\ 7, & 8, & 9 \end{vmatrix}, \quad |B| = \begin{vmatrix} 1, & 4, & 7 \\ 2, & 5, & 8 \\ 3, & 6, & 9 \end{vmatrix},$$

and although these determinants are equal, the matrices A and

* R. H. Fowler, *Journal of the London Mathematical Society*, vol. 1, p. 148, 1926.

† For a useful summary of the properties of matrices, see a review by H. W. Turnbull in the *Mathematical Gazette*, October, 1926. This has been used freely in the description below.

B are different. Technically **B** is called the transposed of **A**. Two matrices are equal only when every element of one is equal to the corresponding element of the other.

Cayley gave rules for adding, subtracting and multiplying matrices. They lead to such results as

$$\begin{aligned} \mathbf{A} + \mathbf{B} &= \mathbf{B} + \mathbf{A} \\ \mathbf{A} + (\mathbf{B} + \mathbf{C}) &= (\mathbf{A} + \mathbf{B}) + \mathbf{C} \\ \mathbf{A}(\mathbf{B} + \mathbf{C}) &= \mathbf{AB} + \mathbf{AC}, \end{aligned}$$

but the product **AB** of two matrices **A** and **B** is not in general equal to the product **BA**.

Here the product **AB** is formed as in multiplying determinants, by weaving the rows of **A** into the columns of **B**, while the product **BA** is formed by weaving the columns of **B** into the rows of **A**. Still using the numerical illustrations, this gives

$$\mathbf{AB} = \begin{bmatrix} 14, & 32, & 50 \\ 32, & 77, & 122 \\ 50, & 122, & 194 \end{bmatrix}, \text{ but } \mathbf{BA} = \begin{bmatrix} 66, & 78, & 90 \\ 78, & 93, & 108 \\ 90, & 108, & 126 \end{bmatrix}$$

For instance in **AB** the first entry 14 is formed from the first row of **A** and the first column of **B**: $(1 \times 1) + (2 \times 2) + (3 \times 3) = 14$. Similarly in **BA** the first entry 66 is formed from the first row of **B** and the first column of **A**: $(1 \times 1) + (4 \times 4) + (7 \times 7) = 66$. Although no physical applications have as yet been attempted, it is perhaps worthy of remark that these methods of treatment may be extended without serious difficulty to arrangements of numbers in three dimensions, so that we may deal with "solid matrices." In fact progress has been made with the general problem of matrices in n dimensions.*

In the classical theory of mechanics a particular co-ordinate may be represented by a Fourier series comprising the various components, but in Heisenberg's theory the collection of all possible vibrations is to be regarded as a whole. The components of a co-ordinate are of the type $A(m, n) e^{i\omega(m, n)t}$, and thus are related naturally to two sets of integers in the proper way for representation by a matrix. The totality of all possible vibrations may be represented in a quadratic scheme forming an infinite matrix,

$$\mathbf{A} = \begin{bmatrix} A(11)e^{i\omega(11)t} & A(12)e^{i\omega(12)t} & \dots \\ A(21)e^{i\omega(21)t} & A(22)e^{i\omega(22)t} & \dots \\ \dots & \dots & \dots \end{bmatrix} \quad \text{. ' } 17:12$$

It is assumed that this matrix may be taken to represent in the new mechanics a positional co-ordinate **q** which may be called a "co-ordinate matrix." In ordinary dynamics we have to deal with positional co-ordinates q and impulse co-ordinates p ,

* Vaidyanathaswamy, *Proc. Roy. Soc. Edin.*, vol. 44, p. 168, 1924.

and the corresponding Hamiltonian function H . Born and Jordan generalize this and, dealing in the first instance with systems of one degree of freedom, consider a co-ordinate matrix q , an impulse matrix p , and a Hamiltonian function $H(p, q)$ which is also a matrix. From analogy with classical theory it is assumed that $A(n, m)$ and $A(m, n)$ are conjugate complex quantities. A matrix for which this condition holds has been named "hermitic" after the French mathematician Hermite.

Following the analogy of the classical theory (p. 20) the equations of motion may be written in the form

$$\dot{p} = -\frac{\partial H}{\partial q}, \quad \dot{q} = \frac{\partial H}{\partial p} \quad . \quad . \quad . \quad 17:13$$

It is now necessary to define what is meant by differentiation in dealing with matrices. No difficulty presents itself in differentiating with respect to the time, but the question of defining formal matrix differentiation is less simple. However, an acceptable form can be found, which, although slightly artificial, seems to meet the requirements of the case.

Perhaps the most interesting point arises in the transcription of the quantum condition from the older quantum theory to the new. Quantum multiplication is not commutative, and instead of assuming that the product qp is equal to the product pq , we have now to introduce a new postulate, viz.

$$pq - qp = \frac{h}{2\pi i} \mathbf{1} \quad . \quad . \quad . \quad 17:14$$

where h is Planck's constant, and $\mathbf{1}$ is the unit diagonal matrix

$$\mathbf{1} = \begin{bmatrix} 1 & 0 & 0 & . \\ 0 & 1 & 0 & . \\ 0 & 0 & 1 & . \\ . & . & . & . \end{bmatrix}$$

By way of illustration we may quote the results obtained by the application of the new mechanics to the simple harmonic oscillator. The Hamiltonian function is of the form

$$H = \frac{1}{2}p^2 + \frac{1}{2}\omega_0^2 q^2 \quad . \quad . \quad . \quad 17:15$$

The canonical equations

$$\dot{q} = p, \quad \dot{p} = -\omega_0^2 q \quad . \quad . \quad . \quad 17:16$$

on elimination of p yield

$$\ddot{q} + \omega_0^2 q = 0 \quad . \quad . \quad . \quad 17:17$$

This can be shown to imply (on putting $\omega_0 = 2\pi\nu_0$)

$$(\nu^2(nm) - \nu_0^2)q(nm) = 0 \quad . \quad . \quad . \quad 17:18$$

The quantum condition in this case takes the form

$$\begin{aligned}\Sigma_k[\nu(nk) - \nu(km)]q(nk)q(km) &= -\frac{h}{4\pi^2} \text{ when } n = m, \\ &= 0 \text{ when } n \neq m.\end{aligned}$$

It follows from the equation of motion that $q(nm)$ can differ from zero only when

$$\nu(nm) = \frac{1}{h}(W_n - W_m) = \pm \nu_0 \quad . \quad . \quad 17:19$$

In any row m of the matrix there can be at most two elements which do not vanish, namely those for which

$$W_n = W_m + h\nu_0 \text{ or } W_n = W_m - h\nu_0.$$

This result implies that we have to deal with an arithmetical series of energy levels which may be described by

$$W_n = W_0 \pm n h \nu_0.$$

From the quantum condition we obtain the result

$$\begin{aligned}\frac{h}{8\pi^2} &= -\Sigma_k \nu(nk) |q(nk)|^2 \\ &= \nu_0 (|q(n, n+1)|^2 - |q(n, n-1)|^2). \quad 17:20\end{aligned}$$

This leads to the relations

$$|q(1, 0)| = \frac{h}{8\pi^2\nu_0}$$

$$|q(n+1, n)|^2 = |q(n, n-1)|^2 + \frac{h}{8\pi^2\nu_0} \quad n = 1, 2, 3 \dots$$

and so

$$|q(n+1, n)|^2 = (n+1) \frac{h}{8\pi^2\nu_0} \quad . \quad . \quad 17:21$$

These values apply in the matrix specifying q

$$q = \begin{bmatrix} 0 & q(0, 1)e^{i\omega(0, 1)t} & 0 & 0 & \dots \\ q(1, 0)e^{i\omega(1, 0)t} & 0 & q(1, 2)e^{i\omega(1, 2)t} & 0 & \dots \\ 0 & q(2, 1)e^{i\omega(2, 1)t} & 0 & q(2, 3)e^{i\omega(2, 3)t} & \dots \\ \dots & \dots & \dots & \dots & \dots \end{bmatrix} \quad 17:22$$

Also we find

$$H(n, n) = h\nu_0(n + \frac{1}{2}) \quad . \quad . \quad . \quad 17:23$$

As compared with the classical quantum theory we find the extra constant term $\frac{1}{2}h\nu_0$ representing what we may call a "zero-point" energy.

The development of the new theory is taking place with great rapidity, and several applications have already proved successful: only a few of these can be mentioned here. Pauli has shown that the Balmer formula for the hydrogen spectrum can be accounted for quantitatively, as well as the influence of

electric and magnetic fields on this spectrum. Brillouin has treated the subject of rotation spectra by the calculus of matrices and has found experimental verification for certain of the theoretical deductions. Dirac has discussed the extension of the theory to relativity mechanics, and in particular to the theory of Compton scattering and obtained results which can be tested by experiment.

3. The Quantum Algebra of Dirac

Independently of Born and Jordan the work of Heisenberg has been developed by P. A. M. Dirac * whose method is somewhat more general and may be described as a quantum algebra. Let x and y be two quantum variables as employed by Heisenberg. Then the sum of x and y is determined by the equation

$$\{x + y\}(nm) = x(nm) + y(nm) \quad . \quad . \quad 17:24$$

and the product by

$$xy(nm) = \sum_k x(nk)y(km) \quad . \quad . \quad 17:25$$

The quantity with components thus defined is called the Heisenberg product of x and y , and may be written simply as xy .

In general $xy \neq yx$ and quantum multiplication is not commutative, although it is associative and distributive.

Dirac then proceeds to quantum differentiation and considers from the start what significant formal definitions of differentiation are possible in the new algebra. The operation d/dv must satisfy the two laws

$$\left. \begin{aligned} \text{and} \quad \frac{d}{dv}(x + y) &= \frac{d}{dv}x + \frac{d}{dv}y \quad . \quad . \quad . \quad \text{I} \\ \frac{d}{dv}(xy) &= \frac{d}{dv}x \cdot y + x \cdot \frac{d}{dv}y \quad . \quad . \quad \text{II} \end{aligned} \right\} \quad . \quad 17:26$$

the order of x and y being preserved in the last equation.

The conclusion which he reaches is that the most general operation satisfying the laws I and II is

$$\frac{d}{dv}x = xa - ax \quad . \quad . \quad . \quad 17:27$$

where a is another quantum variable. Thus the operation of differentiating a quantum variable is equivalent to taking the difference of its Heisenberg products with some other quantum variable. The significance of this result is very great, for it throws light upon the occurrences of differences in the new algebra where we find differentials in classical theory. It must

* P. A. M. Dirac, *Proc. Roy. Soc.*, vol. 109, p. 642, 1925; vol. 110, p. 561, 1926; vol. 112, p. 661, 1926; vol. 113, p. 621, 1927.

of course be remembered that the new method was designed with this end in view.

In classical mechanics certain expressions occur of the form

$$\sum r. \left\{ \frac{\partial x}{\partial q_r} \frac{\partial y}{\partial p_r} - \frac{\partial y}{\partial q_r} \frac{\partial x}{\partial p_r} \right\},$$

where the p 's and q 's are any set of canonical variables of the system. Such an expression is called a "Poisson bracket expression" (P.B.), and it may be denoted by $[x, y]$.

Poisson brackets satisfy the equations

$$\begin{aligned} [x + y, a] &= [x, a] + [y, a]; \\ [xy, a] &= x[y, a] + [x, a]y; \\ \dot{x} &= [x, H]. \end{aligned}$$

The form of the result for the differentiation of a quantum variable suggests a comparison of $xa - ax$ with the Poisson bracket expression of classical theory.

Dirac is led to make as a fundamental basis for the new mechanics the assumption:

$$xy - yx = \frac{i\hbar}{2\pi} [x, y] \quad . \quad . \quad . \quad 17:28$$

or the difference between the two Heisenberg products of two quantum quantities is equal to $i\hbar/2\pi$ times their Poisson bracket expression.

If p_r, q_r are any set of canonical variables of the classical system, this postulate gives

$$\begin{cases} q_r q_s - q_s q_r = 0, & p_r p_s - p_s p_r = 0 \\ q_r p_s - p_s q_r = 0 \quad (r \neq s), & q_r p_r - p_r q_r = (i\hbar/2\pi)(1) \end{cases} \quad . \quad 17:29$$

These equations are the "quantum conditions" of the new mechanics. They are equivalent to the conditions proposed by Born, Heisenberg and Jordan.

The equations of motion are

$$\dot{x} = [x, H] = \frac{2\pi i}{\hbar} [Hx - xH] \quad . \quad . \quad . \quad 17:30$$

and in all cases $\dot{H} = 0$.

In a later paper Dirac generalizes the results given above. The matrix representation is only suitable in dealing with a multiply periodic system, where it plays much the same part as Fourier series in classical mechanics. Dirac points out that as the variables used for describing a dynamical system do not satisfy the commutative law, they are not "numbers" in the sense of the word previously used in mathematics. He therefore calls them q -numbers, and the numbers of classical mathematics c -numbers. At present it is not possible to form a picture of what a q -number is like, but we suppose such numbers satisfy all the ordinary laws of algebra, excluding the commutative law

of multiplication. To obtain from our theory results which may be compared with experiment we require some way of representing q -numbers by means of c -numbers, so that we can compare these c -numbers with experimental values. But even when there is at present no way of representing a q -number by means of c -numbers, the q -number still has a meaning, and can be used in analysis. The quantum conditions previously given apply in this case if we now interpret the symbols as representing q -numbers, not necessarily matrices. The equations of motion are assumed to be

$$\dot{x} = \frac{2\pi i}{h} (Hx - xH),$$

x , $\dot{x}$ and H being all q -numbers.

Dirac discusses in terms of the new mechanics the orbital motion in the hydrogen atom, a problem which has also been treated by Pauli. He assumes that the Hamiltonian for the hydrogen atom is the same function of the Cartesian co-ordinates and their corresponding momenta as on the classical theory. (If polar co-ordinates are employed in similar fashion the results do not agree with experiment.) The investigation shows that, subject to a certain assumption as to the normal state of the atom, the transition frequencies found are the observed frequencies of the hydrogen spectrum.

In discussing the relation between the quantum theory and the classical laws Dirac remarks that the new theory "suggests that it is not the equations of classical mechanics that are in any way at fault, but that the mathematical operations by which physical results are deduced from them require modification. All the information supplied by the classical theory can thus be made use of in the new theory."

4. The Undulatory Mechanics of Schrödinger

An undulatory theory of the mechanics of atoms and molecules has been advanced by Schrödinger,* based on the researches of Louis de Broglie on "phase-waves," which are thought to be associated with the motion of material points (atoms or electrons). The point of view taken by Schrödinger is rather that "material points consist of, or are nothing but, wave-systems." This is no doubt going from one extreme to the other, but in view of the difficulties met with in the ordinary theory of atomic

* Schrödinger, *Ann. d. Physik*, vol. 79, pp. 361, 489, 734; vol. 80, p. 437; vol. 81, p. 109, 1926. The account of the theory given here is based mainly on an article in the *Physical Review*, vol. 28, p. 1049, 1926. Since this was written, "an introductory sketch," entitled *Wave Mechanics*, has been published by H. F. Biggs (Oxford University Press, 1927).

mechanics, it seems desirable, at least for a time, to lay what is perhaps an exaggerated stress on its counterpart.

The relation between these two theories shows a striking analogy to the relation between geometrical optics and physical optics. The mechanical conception of the path or orbit of a material particle corresponds to the conception of a ray of light in optics. Now the conception of rays is restricted to pure abstract geometrical optics, and loses nearly all its significance in physical optics. It breaks down as soon as the dimensions of the beam, or of material obstacles in its path, become comparable with the wave-length. It is incapable of being applied to such phenomena as those of diffraction without the addition of such extraneous ideas as that of Huyghens' principle, and even when extended in this way, certain arbitrary rules have to be laid down in the construction of "Fresnel's zones." Geometrical optics can be regarded as the limiting case of undulatory optics for vanishingly small wave-length.

Now we know that ordinary mechanics is not applicable to mechanical systems of very small (atomic) dimensions. The question suggests itself whether the non-applicability of ordinary mechanics to such systems is not of exactly the same kind as the non-applicability of geometrical optics to the phenomena of diffraction or interference, and may perhaps be overcome in an exactly similar way.

Bohr's theory represents a complete departure from ordinary mechanics. When we come to deal with these atomic systems the laws of classical mechanics seem to fail us. Schrödinger suggests that this may be because we are not really concerned in these systems with material points obeying ordinary dynamical laws. We may be concerned with some motion having the attribute of frequency or wave-length, and if this be the case, our difficulties may arise because this wave-length is comparable with the dimensions of the atom.

To explain the main lines of thought, consider a material point of mass m , moving in a conservative field of force, $V(x, y, z)$.

The kinetic energy T is, in the usual notation,

$$T = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) \quad . \quad . \quad . \quad \text{I7:31}$$

or it may be written

$$T = \frac{1}{2m}(\dot{p}_x^2 + \dot{p}_y^2 + \dot{p}_z^2) \quad . \quad . \quad . \quad \text{I7:32}$$

where $\dot{p}$ stands for momentum ($\dot{p}_x = m\dot{x}$, $\dot{p}_y = m\dot{y}$, $\dot{p}_z = m\dot{z}$). The well-known Hamiltonian function of action, called by Schrödinger W , is defined by the equation

$$W = \int_{t_0}^t (T - V) dt \quad . \quad . \quad . \quad \text{I7:33}$$

taken as a function of the upper limit t and of the final values of the co-ordinates x, y, z . This satisfies the Hamiltonian partial differential equation

$$\frac{\partial W}{\partial t} + \frac{1}{2m} \left[\left(\frac{\partial W}{\partial x} \right)^2 + \left(\frac{\partial W}{\partial y} \right)^2 + \left(\frac{\partial W}{\partial z} \right)^2 \right] + V(x, y, z) = 0 \quad 17:34$$

To solve this differential equation we put

$$W = -Et + S(x, y, z) \quad . \quad . \quad . \quad 17:35$$

E being an integration constant, namely, the total energy, and S a function of x, y, z only. We can write the equation in the form :

$$\left[\left(\frac{\partial W}{\partial x} \right)^2 + \left(\frac{\partial W}{\partial y} \right)^2 + \left(\frac{\partial W}{\partial z} \right)^2 \right] = 2m(E - V) \quad . \quad 17:36$$

Here $\frac{\partial W}{\partial x}$, $\frac{\partial W}{\partial y}$ and $\frac{\partial W}{\partial z}$ are the components of the gradient of W in the direction of the axes, and so symbolically we may write the equation

$$|\text{grad. } W| = [2m(E - V)]^{\frac{1}{2}} \quad . \quad . \quad . \quad 17:37$$

This equation may be given a simple geometrical interpretation. Assume t constant for the moment. Then the equation $W = W_0$ defines a surface in space for which W assumes a constant value W_0 . We may imagine a series of such surfaces corresponding to arbitrary values of W , and when the time is allowed to vary, we may think of the surfaces as wandering in space in such a way that each of them continually takes the place and exact form of the neighbouring surface. It can be shown that the normal-velocity of any surface at any one of its points is given by

$$u = E/[2m(E - V)]^{\frac{1}{2}} \quad . \quad . \quad . \quad 17:38$$

This picture exactly coincides with the propagation of a stationary wave-system in an optically non-homogeneous (but isotropic) medium, W being proportional to the phase, and u being the phase velocity.

Now let us associate with the system of W -surfaces the idea of stationary sinusoidal waves whose phase is given by W . There will be a certain wave function, represented by Schrödinger by ψ , and this will be of the form

$$\psi = A(x, y, z) \sin(W/K) \\ \therefore \psi = A(x, y, z) \sin \left[-\frac{Et}{K} + \frac{S(x, y, z)}{K} \right] \quad . \quad 17:39$$

It is necessary to introduce the constant K having the physical dimensions of *action*, since the argument of a sine must always be a pure number.

The frequency of the waves is given by

$$\nu = E/2\pi K \quad . \quad . \quad . \quad 17:40$$

Schrödinger says: "One cannot resist the temptation of supposing K to be a *universal constant*, independent of E and independent of the nature of the mechanical system, because if this be done, and K be given the value $h/2\pi$, then the frequency will be given by

$$\nu = E/h \quad . \quad . \quad . \quad . \quad . \quad 17:41$$

h being Planck's constant. Thus the well-known universal relation between energy and frequency is arrived at in a rather simple and unforced way."

The wave-length of the waves is

$$\lambda = u/\nu = h/[2m(E - V)]^{1/2} \quad . \quad . \quad . \quad 17:42$$

Here $E - V$ is the kinetic energy, and for our single particle this is equal to $\frac{1}{2}mv^2$, which is independent of the zero-level of the total energy. Inserting this value we find $\lambda = h/mv$. It follows from this that when an electron is moving in an orbit of atomic dimensions, the wave-length must be of the same order of magnitude as the size of the orbit. Consequently ordinary mechanics will be no more applicable to such an orbit than geometrical optics is to the diffraction of light by a disc of diameter equal to the wave-length. For an orbit of high quantum number the ratio of wave-length to orbital dimensions diminishes and ordinary mechanics offers a better approximation.

In the application of the theory to micro-mechanical problems it is necessary to use an "equation of wave propagation." For example, when a single material point moves in an external field of force Schrödinger finds that we may use the wave-equation:

$$\Delta\psi - \dot{\psi}/u^2 = 0 \quad . \quad . \quad . \quad . \quad 17:43$$

and insert for u the quantity previously given. This velocity u depends on the space co-ordinates because it contains V , and on the frequency because it contains E/h . The latter condition implies that ψ the wave function is harmonic with respect to the time, and therefore contains the factor $e^{\pm 2\pi i t E/h}$.

Therefore we have

$$\ddot{\psi} = -4\pi^2 E^2 \psi / h^2 \quad . \quad . \quad . \quad . \quad 17:44$$

Substituting this value in the equation of wave propagation we get

$$\Delta\psi + 8\pi^2 m(E - V)\psi/h^2 = 0 \quad . \quad . \quad 17:45$$

For the simplified hydrogen atom composed of proton and electron we put $V = -e^2/r$, and thus obtain the equation

$$\Delta\psi + 8\pi^2 m(E + e^2/r)\psi/h^2 = 0 \quad . \quad . \quad 17:46$$

The solution * of this equation, then, depends on the value of

* Eddington (*Nature*, vol. 120, p. 117, 1927) has pointed out that the solution of Schrödinger's differential equation for this problem is treated in Whittaker and Watson's *Modern Analysis*, Chapter XVI, and that the task of determining the "eigenvalues" and "eigenfunctions" may be made easier for English readers by employing Whittaker's function.

E. It turns out that the only E values for which solutions exist that are continuous, finite and single-valued throughout the whole space are the following :

$$(1) E > 0.$$

$$(2) E = -2\pi^2 m e^4 / h^2 n^2 \quad (n = 1, 2, 3, 4 \dots) \quad \dots \quad 17:47$$

The first set of solutions corresponds to the hyperbolic orbits in ordinary mechanics. It is indeed remarkable that in this method of treatment these orbits appear quite spontaneously from the fact that every positive value of E leads to finite solutions. But what is even more remarkable is that the second set corresponds exactly to Bohr's stationary energy levels of the circular or elliptic orbits. The selected values of E may be named "characteristic values" (Eigenwerte), and the solutions of the equation for ψ belonging to them "characteristic functions."

Schrödinger gives an interesting discussion of the question why the equation for ψ should possess finite solutions only for certain selected values of the constant E. Briefly it may be stated that the first set of E values, $E > 0$, makes the square of the phase-velocity positive throughout the space, the second set makes this quantity negative. In the latter case "there is in the course of time a tendency to exaggerate infinitely all 'humps' of the function and even spontaneously to form humps out of quite insignificant traces. Evidently a function which is subject to such a revolutionary sort of equation, is continually exposed to the very highest danger of increasing or decreasing beyond all limit. At any rate it is no longer astonishing that special conditions must be fulfilled to prevent such an occurrence. The mathematical treatment shows that these conditions consist exactly in E having one of the second set of characteristic values."

Another problem which may be solved by the methods of undulatory mechanics is that of the harmonic oscillator. This yields for the E levels the values $(n + \frac{1}{2})h\nu_0$ (where in this case n may take the values 0, 1, 2, 3, 4 . . .) instead of $n h \nu_0$ as in the ordinary quantum theory. There is, then, this additional term $\frac{1}{2}h\nu_0$ corresponding to what was suggested as being a zero-point energy in some of the previous theories.

Another interesting problem solved by the new method is that of a rotating body such as a molecule. If this body have moment of inertia I, the E levels are given by $n(n + 1)h^2/8\pi^2 I$. In the ordinary theory instead of $n(n + 1)$ we get n^2 .

In our actual observations we are interested only in differences of level, and in this case the new formula amounts to the same as replacing n^2 by $(n + \frac{1}{2})^2$, for $(n + \frac{1}{2})^2 - n(n + 1) = \frac{1}{4}$,

which is a constant and so disappears when we are considering differences of levels. It may be recalled that so-called half-quantum numbers have been employed for some time in connection with band spectra.

Fues * has worked out the band theory of diatomic molecules in detail, taking into account the mutual influence of rotation and oscillation and also the fact that the oscillation is not of the simple harmonic type. The result is in exact agreement with the ordinary treatment except that the quantum numbers become half-integral also in all correction terms.

A theory of the Stark effect based on Schrödinger's ideas has been presented by Epstein † who considers the radiation from a hydrogen-like atom in an electric field. After a general mathematical exposition of the method, the positions of the components are determined to terms of the second order in the electrical field. The positions of the lines practically coincide with those obtained in Epstein's old theory which gave excellent agreement with experiment. The main interest lies in the expressions for the intensities, which are simple in their structure and agree with the observed values better than the expressions derived by Kramers from Bohr's correspondence principle. A further point of interest is that components which, in the old theory, had to be ruled out by a special postulate, now drop out automatically. Schrödinger himself has discussed the same problem and obtained similar results.

A generalized operator calculus for dealing with the equations of quantum dynamics has been developed by Carl Eckart ‡, who claims that it leads to methods of solution much simpler than those previously given. Born and Wiener § had previously shown that the matrices were closely related to a special form of operator, and that the operator calculus furnished a means of calculating the matrices. Eckart shows that the results of Schrödinger may be included in the matrix calculus of Born and Jordan, thus giving an independent confirmation of Schrödinger's own presentation || (based on his wave-mechanics) of the mathematical equivalence of the two theories.

An interesting suggestion as to the physical meaning of the wave-function ψ has been made by Schrödinger. Let $\bar{\psi}$ denote a conjugate complex value. Then $\psi\bar{\psi}$ is the square of the absolute value of the complex function ψ and in the case of the hydrogen atom is proportional to the charge of the electron,

* Fues, *Ann. d. Physik*, vol. 80, p. 367, 1926.

† Epstein, *Phys. Rev.*, vol. 28, p. 659, 1926.

‡ Carl Eckart, *Phys. Rev.*, vol. 28, p. 711, 1926.

§ Born and Wiener, *Zeits. f. Physik*, vol. 36, p. 174, 1926.

|| Schrödinger, *Ann. d. Physik*, vol. 79, p. 734, 1926.

which is to be regarded not as concentrated in a point but as spread throughout space. As the wave-function ψ practically vanishes not far from the nucleus, the charge is actually restricted to a domain of, say, a few Angstroms. It is possible to extend this idea to the more general case of several electrons. Thus the wave-function physically means and determines a continuous distribution of electricity in space, the fluctuations of which determine the radiation by the laws of ordinary electrodynamics.

Further evidence in favour of the connection between the field scalar ψ and the electric density of the current has been given by Fermi.* He has shown that Schrödinger's hypothesis leads to the right expression for the magnetic moment of a hydrogen-like atom. He considers only the part of the magnetic moment which, in the old quantum theory, was supposed to be due to the orbital motion of the electron, leaving the magnetic moment of the spinning electron to be considered separately. The wave equation for a hydrogen-like atom in a magnetic field has been integrated by Fock,† and it appears from his solution that the lines of current are circles situated in planes perpendicular to the axis and with their centres on the axis. It is hence shown that the component of the magnetic moment in the direction of the field is the product of a Bohr magneton and the magnetic quantum number of the old theory. It is noteworthy that this magnetic moment arises in a certain way through the action of the field in which the atom is situated.

In view of this result it seems safe to infer that the number of quantum magnetic tubes of induction associated with the atom in this state is equal to the magnetic quantum number.

It is of interest to find that there appears to be a possibility of correlating wave mechanics with Maxwell's theory. This question has been discussed by Bateman,‡ de Broglie,§ and Carrelli.|| Functions can be found satisfying the wave equation and giving for the electric and magnetic fields the values characteristic of an electric pole of assigned charge. It is also possible to introduce the spinning electron into the theory, and obtain expressions for the electric and magnetic fields due to a spinning charge which is equivalent as regards the magnetic field to a magnetic dipole.

We have referred in Chapter XI to the five-dimensional theory of Kaluza and Klein. The relation of this theory to the undulatory mechanics of Schrödinger has been discussed by Klein

* Fermi, *Nature*, vol. 118, p. 876, 1926.

† Fock, *Zeits. f. Physik*, vol. 38, p. 242, 1926.

‡ Bateman, *Nature*, vol. 118, p. 839, 1926.

§ de Broglie, *C.R.*, vol. 184, p. 81, 1927.

|| Carrelli, *Nature*, vol. 119, p. 492, 1927.

and by others.* It has been shown by Ehrenfest and Uhlenbeck† that a graphical representation of the phase waves of de Broglie may be obtained in the five-dimensional universe.

A remarkable result which indicates an inner unity between the quantum theory and gravitational relativity has been announced by Wiener and Struik.‡ The connecting link is the wave theory of Schrödinger. If we define the gravitational field in the proper invariantive manner in terms of a wave equation, the quantization of this equation follows from the gravitational field equations. The equation also defines an electromagnetic potential, to which most of Weyl's considerations apply.

The fundamental equation of these authors can be rendered homogeneous by means of a suitable substitution, and a treatment of their theory is then obtained analogous to that of Klein. "The fifth dimension turns out to be a mere mathematical convention that can be compared to the introduction of homogeneous co-ordinates in other parts of mathematics."

One test of a scientific theory is its comprehensiveness, and the wide sweep of the new quantum mechanics is shown not only in the various ways of formulating it in mathematical language, but also in the physical ideas that may be associated with it. It is probable that the views of the quantum suggested by Whittaker and by the present writer, in which its magnetic aspects are emphasized, may be simply related to the new theory. In a recent paper Whittaker has described a simple light quantum in which a disembodied magnetic molecule, travelling with the speed of light, forms a singularity on the wave front and confers upon it the desired quantum properties. It may be suggested that such a quantum is related to a quantum magnetic tube on the one hand, and to Schrödinger's wave mechanics on the other.

5. Statistical Methods and the Quantum Theory

The application of probability methods in quantum theory has attracted considerable attention since the publication of an important paper by Einstein § in 1917. He showed that Planck's radiation law could be derived by considering the probability of transitions between different stationary states, assuming Bohr's frequency condition to hold for the radiation emitted or absorbed in a transition. He considered an enclosure containing a gas,

* Klein, *Zeits. f. Physik*, vol. 37, p. 895, 1926; Fock, *Zeits. f. Physik*, vol. 39, p. 226, 1926; Gamow and Iwanenko, *Zeits. f. Physik*, vol. 39, p. 865, 1926; Iwanenko and Landau, *Zeits. f. Physik*, vol. 40, p. 161, 1926.

† Ehrenfest and Uhlenbeck, *Zeits. f. Physik*, vol. 39, p. 495, 1926.

‡ Wiener and Struik, *Nature*, vol. 119, p. 853, 1927.

§ Einstein, *Phys. Zeits.*, vol. 18, p. 122, 1917. See Birtwistle, *Quantum Theory*, p. 36.

the atoms of which could assume a number of stationary states, and investigated the equilibrium subsisting between the atoms and the surrounding radiation. In thermodynamic equilibrium between the atoms and the radiation, the number of elementary processes in one direction ought to balance the number occurring in the opposite direction. This condition gives a formula expressing the energy density of the radiation in terms of the probability coefficients introduced by Einstein. The truth of Boltzmann's formula for the relative number of systems in different states of energy in an assemblage at given temperature is assumed, and use is made also of Wien's displacement-law. It is to be observed that although Einstein endeavoured to give a derivation which should be independent of classical theory, he had to employ certain classical results. Eddington* has shown that it is unnecessary to assume Boltzmann's formula; this, as well as Planck's law, can be deduced directly from Einstein's equation.

Einstein's method has been applied by Milne† to the photo-electric effect, and the formulæ obtained for the photo-electric activity of radiation agree with those developed by Kramers‡ and have a very close connection with formulæ deduced by Richardson§ prior to the publication of Bohr's theory.

Bose|| has given a method of deriving Planck's law which is independent of the classical theory. He employs the light quantum hypothesis and concludes that the phase-space of a light quantum is divided into "cells" of size h^3 . Considering a particular type of radiation, the number of possible arrangements of the light quanta into these "cells" represents a certain "probability." The thermodynamic probability of a macroscopic state is calculated, and therefrom the entropy. Thus the thermodynamic characteristics of the radiation are determined, and a formula is obtained which is the equivalent of Planck's law. Einstein¶ emphasized the importance of the method and showed that it might be applied to the quantum theory of an ideal gas containing structureless mass-points. According to his views a light quantum (apart from its polarization property) differs from a monatomic molecule only in the fact that the static mass of the quantum is vanishingly small. This new form of statistical mechanics has been further analysed by Schrödinger,** who states that the precise meaning of the Einstein gas theory is that a gas may be considered as a system of separate

* Eddington, *Phil. Mag.*, vol. 50, p. 803, 1925.

† Milne, *Phil. Mag.*, vol. 47, p. 209, 1924.

‡ Kramers, *ibid.*, vol. 46, p. 836, 1923.

§ Richardson, *ibid.*, vol. 47, p. 975, 1924.

|| Bose, *Zeits. f. Physik*, vol. 26, p. 178, 1924.

¶ Einstein, *Preuss. Akad. Wiss. Berlin*, 22, p. 261, 1924; 1, pp. 3, 18, 1925.

** Schrödinger, *Phys. Zeits.*, vol. 27, p. 95, 1926.

linear vibrations, similar to those in a solid body, or in an enclosure containing radiation.

The quantization of the monatomic perfect gas has been discussed by Fermi.* If the heat theorem of Nernst is to hold good for the ideal gas it is necessary to assume that at low temperatures the laws for an ideal gas deviate from the classical laws. This deviation is attributed to the "degeneration" of the gas, and according to Fermi its cause is to be sought in the quantization of the molecular motions. It is necessary to distinguish between this type of deviation and the deviation due to the fact that the gas is real and not perfect, the former having hitherto been masked by the latter under experimental conditions. The equation of state and the internal energy of the ideal gas are deduced by employing the hypothesis of Pauli, which for the purpose in hand may be stated in the form that one system can never contain two elements of equal value having their quantum numbers in absolute agreement.

Results of a similar character have been obtained independently by Dirac,† whose work is based on the new quantum mechanics. It has been shown both by Dirac and by Heisenberg ‡ that Pauli's principle and its extension are satisfied in the new mechanics by a complete self-consistent solution of the equations of motion. Fowler § has employed the method of complex integration in an examination of a quite general form of statistical mechanics of which the classical form and Einstein's and Fermi-Dirac's are special cases.

In a later paper Dirac || has treated the problem of an assembly of similar systems satisfying the Einstein-Bose statistical mechanics, which interact with another different system, a Hamiltonian function being obtained to describe the motion. The theory is applied to the interaction of an assembly of light-quanta with an ordinary atom, and it is shown that it gives Einstein's laws for the emission and absorption of radiation.

The interaction of an atom with radiation is also considered, assuming the radiation composed of electromagnetic waves. It is shown that a Hamiltonian function can be obtained of the same form as in the light-quantum treatment. The wave point of view is thus consistent with the light-quantum point of view. The theory leads to the correct expressions for the probability coefficients both for the absorption process and for the emission process (Einstein's A's and B's).

* Fermi, *Rend. Acc. Lincei*, ser. 6, vol. 3, p. 145, 1926; *Zeits. f. Physik*, vol. 36, p. 902, 1926.

† Dirac, *Proc. Roy. Soc.*, vol. 112, p. 661, 1926.

‡ Heisenberg, *Zeits. f. Physik*, vol. 38, p. 411, 1926.

§ Fowler, *Proc. Roy. Soc.*, vol. 113, p. 432, 1926.

|| Dirac, *Proc. Roy. Soc.*, vol. 114, p. 243, 1927.

CHAPTER XVIII

THE INTERPRETATION OF THE QUANTUM

From the point of view of the physicist, a theory of matter is a policy rather than a creed ; its object is to connect or to co-ordinate apparently diverse phenomena, and above all to suggest, stimulate, and direct experiment.

J. J. THOMSON, *The Corpuscular Theory of Matter*, p. 1, 1907

Grant I have mastered learning's crabbed text,

Still there's the comment.

Let me know all ! Prate not of most or least,

Painful or easy !

Even to the crumbs I'd fain eat up the feast,

Ay, nor feel queasy.

ROBERT BROWNING, *A Grammarian's Funeral*

1. The Meaning of "Explanation" in Physics

IN attempting to review the suggestions that have been made as to the interpretation of the quantum, it may be well to consider at the outset what exactly is implied in physical science by such a term as "explanation" or "interpretation." In ordinary language we speak of explanation when some strange or unfamiliar phenomenon is expressed in terms of processes or events which are familiar to us, and are called well-known, though we may be, and often are, in ignorance of their true character. The concept of "explanation" must pass through a process of evolution with the progress of knowledge. "To explain a phenomenon is, for primitive man, to interpret it anthropomorphically by a supernatural agent endowed with psychological life in his own image ; for a scholastic it is to explain it by ultimate causes ; for Bacon to explain it by efficient causes ; for Maxwell it is to deduce it from the principles of mechanics ; for Gibbs and Boltzmann it is to account for it by the calculus of probabilities, by starting from a system of elements subject to given conditions." *

In modern scientific work we are said to explain phenomena when we show that they can be expressed as examples of certain general "laws" which have come to be recognized as holding in

* Rougier, *Philosophy and the New Physics*, p. 146 (Routledge).

a large number of instances, or when we regard them as results which follow from some theory which is known to embrace many facts of observation or experiment.

"Explanation of a fact can mean no more than this, correlation with and co-ordination among an existing body of other facts which can all be similarly related to the same general principle. This, however, is enough" (R. H. Fowler).

This method of answering questions by showing that they may be included in a more general category—a method at least as old as our oldest literature—is well illustrated by Clerk Maxwell's "explanation" of light as an electromagnetic disturbance propagated in a medium possessing certain characteristic electric and magnetic properties. Here we are no longer passing from the unknown to the familiar, we might even be said to be turning from a region which is well-known to one which is recondite and strange. But by taking this step we are able to secure a more comprehensive theory which includes under one head two types of phenomena—light and electromagnetic waves—which had previously been considered distinct. The opposition felt by certain physicists, including Lord Kelvin, to the electromagnetic theory of light is reflected in the Preface to the first edition of Schuster's *Optics*, 1904, which begins with the words: "There is at present no theory of Optics in the sense that the elastic solid theory was accepted fifty years ago. We have abandoned that theory, and learned that the undulations of light are electromagnetic waves differing only in linear dimensions from the disturbances which are generated by oscillating electric currents or moving magnets. But so long as the character of the displacements which constitute the waves remains undefined we cannot pretend to have established a theory of light."

The view that the real nature of phenomena will never be understood led Wilhelm Ostwald, who for a long period withheld his allegiance from the atomic theory, to his philosophy of "Energetics," but even Ostwald in his later years was compelled to avow his belief in the discrete or grained structure of matter. "The isolation and counting of gaseous ions on the one hand . . . and on the other the agreement of the Brownian movements with the requirements of the kinetic hypothesis . . . justify the most cautious scientist in now speaking of the experimental proof of the atomic theory of matter. The atomic hypothesis is thus raised to the position of a scientifically well-founded theory."

Poincaré also in his last scientific book, was forced to the same conclusion. "The atoms are no longer a convenient fiction; it seems to us that we can, so to speak, see them, since we know how to count them."

The marvellous method, due to C. T. R. Wilson, of rendering visible and of photographing the track of a single atomic projectile or a single electron; the scintillations due to alpha particles observed in the spinthariscopes of Crookes; the beautiful experiments of Rutherford and Geiger in which these particles are counted by an ionization method; all these afford convincing evidence for the existence of discrete entities which may be called atoms of matter or of electricity.

More recent photographs taken by Wilson's method, in particular those showing the ionization produced by a beam of X-rays, might almost be said to reveal the existence of quanta, or at least to afford such striking evidence in their favour that even the most sceptical must find it hard to disbelieve.

The controversy between the Realist and the Idealist schools of philosophy which has long been raging is reflected in the antagonistic views of scientific workers. British physicists, inspired by the genius of Newton and influenced by many later teachers, have long sought to develop a mechanical theory of natural phenomena. They have been accustomed to work by means of mechanical models, and as is well known both Faraday and Maxwell made extensive use of such models.

Opposed to this procedure is what may be called the Continental method, which does not attach great importance to models, but prefers to work after the manner of the pure mathematician by means of abstract symbols. Instead of dealing with "action through a medium," investigators of this school recognize "action at a distance" and develop the consequences of that view.

To quote again from Schuster: "Those who believe in the possibility of a mechanical conception of the universe and are not willing to abandon the methods which from the time of Galileo and Newton have uniformly and exclusively led to success, must look with the gravest concern on a growing school of scientific thought which rests content with equations correctly representing numerical relationships between different phenomena, even though no precise meaning can be attached to the symbols used. The fact that this evasive school of philosophy has received some countenance from the writings of Heinrich Hertz renders it all the more necessary that it should be treated seriously and resisted strenuously."

On the other hand we have such a statement as "Maxwell's theory is contained in Maxwell's equations," and we meet those who regard the idea of a real kinetic theory of matter—at one time firmly believed in—as a "mirage." Influenced by the philosophy of "positivism" there is "a school of physics that takes no interest in a mechanism explaining the phenomena, but

describes simply, in its equations, the relations which connect the simultaneous variations of directly measurable physical quantities." * This attitude of reserve may be prudent, but by excluding all explanatory theories it "condemns us to an intellectual asceticism." The human mind cannot permanently remain satisfied with a mere catalogue of relations, and though doomed to disappointment in the search, strives to reach a more comprehensive explanation.

There is no doubt profound truth in the statement of Sir Joseph Larmor: † "In ultimate logic any physical representation is in fact a mental construction or analogy, designed to relieve the mind from the intangible and elusive character of a complex of abstract relations." But such a statement should rather encourage than prohibit attempts at physical representation.

Sir Oliver Lodge has protested against "a comparatively recent anti-scientific tendency to teach that we are not making an attempt to ascertain actual truth about the universe, but only to formulate propositions that are practically helpful and convenient." ‡ Is there then no ultimate scientific certainty? Perhaps an answer to this question may be given by adopting words that have been used in another connection and saying that natural philosophy provides us with "an image, in mind, of a reality previously existing." The image may vary in different minds and in different generations, but it seems almost a necessity of human thought that there must be some reality behind our imaginings. "Truth is in the ideal. The actual world is an approximation thereto. . . . We always aim at truth beyond the range of our experience or measuring achievements. Absolute truth may be an unattainable ideal, but it is our clear and permanent aim." §

2. The Quantum

The problem of the quantum is not single but complex. In its inception the quantum theory was concerned with only one department of physics, but we have come to see that all branches of physics in which small-scale phenomena are investigated are concerned with quantum laws. The nature of radiation, the structure of the atom, the very existence of electric charges and the characteristics of the electro-magnetic field, all are dependent upon the quantum or upon quantum principles.

The feature which forces itself upon our attention in considering the quantum is that of *discontinuity* referred to previously

* See Rougier, *Philosophy and the New Physics* (Routledge).

† Larmor, *Aether and Matter*, p. 334.

‡ Oliver Lodge, *Nature*, vol. 119, p. 423, 1927. § *loc. cit.*

in Chapter XI. "The theories of electricity and thermodynamics which are actually current show a tendency to substitute the discontinuous for the continuous; the hypothesis of quanta seems to explain phenomena better than hypotheses based on continuity. Does this mean that we should introduce this discontinuity into geometry itself? The question is perhaps somewhat premature, but we can hardly avoid putting it" (Émile Borel*).

It may be that our conception of continuous motion is an illusion produced by our senses, the apparatus available for perception being too coarse to appreciate the minute jumps which actually constitute observed phenomena. The question has been stated by Poincaré as follows:

"Is discontinuity destined to reign over the physical universe, and will its triumph be final? Or will it finally be recognized that this discontinuity is only apparent, and a disguise for a series of continuous processes? The first observer of a collision thought he was witnessing a discontinuous process, but we know to-day that what he saw was the result of changes which, although very rapid, were continuous."

The final answer to any series of questions is inevitably—"because the world is so constructed." The final representation of the universe to which the quantum theory seems to point is a four-dimensional space-time world of events, in which unexpected (and perhaps in some respects undesirable) flaws or cracks are to be found. As the late Lord Rayleigh once remarked with reference to this very theory: "It is not the question what we may like or dislike, but what the facts demand."

It appears then that we may be compelled to look upon the four-dimensional world as essentially discontinuous in character. In three dimensions we have emphasized the suggestion that the quantum theory points to the existence of discrete tubes of magnetic induction. Applying the same ideas to the four-dimensional tubes of force of Whittaker, we are led to the view that the world of events is not a continuum, but is built up of individual tubes of force or "calamoids." In his Kelvin lecture Jeans has put this idea in picturesque form by saying that the quantum theory represents a quality of the four-dimensional continuum, which is somehow analogous to the scaliness of a crocodile skin.

In considering such revolutionary ideas as are implied in the quantum theory there are two opposite dangers to be guarded against, as Planck has pointed out in the Preface of the second edition of his *Heat Radiation*. "Any one who would make his attitude concerning the hypothesis of quanta depend on whether

* Émile Borel, *Space and Time*, 1926.

the significance of the quantum of action for the elementary physical processes is made clear in every respect or may be demonstrated by some simple dynamical model, misunderstands, I believe, the character and the meaning of the hypothesis of quanta. It is impossible to express a really new principle in terms of a model following old laws." To illustrate this point we may take the suggestion that the quantum theory implies the existence of discrete tubes of magnetic induction. This supposition standing by itself is not sufficient to explain the quantum theory. For although the ordinary laws of electromagnetism be applied to the stationary state of an atomic system (and even in such a state some modification seems necessary), we are not entitled to apply them to the catastrophic change which takes place between two stationary states. We may, for instance, imagine that such a change involves the separation (or addition) of one or more discrete magnetic tubes, but the change cannot be expressed in terms of the classical electromagnetic laws.

Again, Whittaker's attempt to account for quanta by postulating the existence of a magnetic structure in the atom, although extremely suggestive, does not entirely overcome the difficulty pointed out by Planck.

On the other hand there is the danger of departing too far from the older ideas, and in this connection Planck says: "Since nothing probably is a greater drawback to the successful development of a new hypothesis than over-stepping its boundaries, I have always stood for making as close a connection between the hypothesis of quanta and the classical dynamics as possible, and for not stepping outside of the boundaries of the latter until experimental facts leave no other course open." For this reason Planck himself has not adopted the more radical assumption "that any radiant energy whatever, even though it travel freely in a vacuum, consists of individual quanta or cells."

The strange conflict * between the two rival theories of light has been emphasized repeatedly in this volume. There appears to be direct contradiction between the wave theory and the quantum theory of radiation. The former is able to explain the behaviour of light when it is passing through a telescope or is concerned with interference phenomena; the latter is able to account for emission, absorption or photo-electric action. "The energy of the radiation behaves as though it possessed at the same time the opposite properties of extension and localization." †

* See an article by O. D. Chwolson in *Scientia*, vol. 41, p. 31, 1927.

† O. W. Richardson, *Electron Theory of Matter* (2nd edition), p. 507, 1916.

What will be the issue of the struggle? It may happen that one of the two theories will occupy step by step the territory of the other. Schrödinger in 1922 made some progress in this direction when he gave an explanation of Doppler's principle by the theory of quanta. Kramers in 1924 made an attempt to account for the law of dispersion of light by employing Bohr's principle of correspondence. On the other hand, it may happen that some artificial reunion can be effected between the two theories, and several investigators have worked in this direction. Probably, in this conflict as in that between other antagonistic physical theories, a new and more comprehensive theory will be found which will embody the more important principles of the two rivals. It seems that already the work of de Broglie and of Schrödinger is pointing the way towards such an all-embracing theory.

3. Atomic Models

Physicists in general take up the pragmatic standpoint illustrated by the quotation from Sir Joseph Thomson which stands at the head of the present chapter. For them a working theory is a theory that works, in the sense that it co-ordinates known facts and suggests new lines of investigation. But this need not abrogate the quest for a more complete and all-embracing synthesis.

An excellent illustration of the development of theory is afforded by the history of the attempts that have been made to devise a model of the atom. In the older model of Kelvin and J. J. Thomson the electrons were at rest in a sphere of positive electricity. Later on J. J. Thomson devised a kinetic model in which the electrons revolved in orbits controlled by the positive charge. These models served a most useful purpose, especially in providing a physical interpretation of the periodic classification of the elements. Static models, though somewhat out of favour, may still serve a useful purpose, and may even be employed for approximate calculations (Chapter IX). The work of Ritz, though left uncompleted, emphasized the magnetic aspects of the problem of atomic structure, which for a time tended to become somewhat obscured.

The extraordinary success which has attended the theory of the nuclear atom developed by Rutherford must not blind us to the fact that we have here to do with an atomic model, which is probably only a crude representation of the actual facts of intra-atomic structure. The law of the inverse square of the distance on which the model is based may be interpreted in other ways than by the assumption of point charges (Chapter

XII), and as a matter of fact Rutherford and Chadwick have themselves shown that this law fails when the distance is sufficiently diminished.* After the anticipatory work of Nicholson came the bold advance made by Bohr in introducing quantum conditions for the determination of stationary states, and a new hypothesis for determining the amount of radiation emitted or absorbed in a quantum transition.

Although there has been considerable discussion in the past as to the "correctness" of Bohr's atomic model, such a discussion is almost certainly entirely superfluous at the present time when Bohr himself, and many other physicists with him, would probably say that such a model has, for the time being, a heuristic value and serves the purpose of a good working hypothesis. There is, indeed, a tendency in some quarters to go to extremes and discard all attempts at constructing models of the ultimate physical entities. Let us express in mathematical language, say some philosophers, only these results which are capable of actual observation, and put on one side all such mechanistic interpretations as require, for instance, a knowledge of the position in space at a particular instant of time of a particular electron.

The conflict between the rival theories of light which has already been described has its counterpart in the two views which may be taken as to the constitution of matter. These might be somewhat inadequately described as the static and the dynamic views. The wave-theory of matter associated with the names of de Broglie and Schrödinger emphasizes the idea that a mass particle is associated with or is equivalent to a condition of vibration. It may be that the solution of our difficulties in regard to the rival theories, both of radiation and of matter, will eventually be found in a more general theory which will include both radiation and matter in an extended wave mechanics.

4. The New Quantum Mechanics

The new quantum mechanics affords an instructive example of two contrasted methods of attacking a physical problem. The matrix mechanics is based on the principle that only such quantities as are directly open to observation are to be employed in the mathematical formulation; the undulatory mechanics is based on the assumption that an atomic system, composed of electrified particles, may be treated as equivalent to a wave-motion determined by a special form of wave-equation. Although

* See the Twelfth Guthrie Lecture, "Atomic Nuclei and their Transformations," Rutherford, *Proc. Phys. Soc.*, vol. 39, p. 359, 1927.

the two systems of mechanics appear so different in their origin, and in the point of view adopted, they lead to practically identical results, and it has been shown that mathematically they are almost equivalent. To the physicist the wave mechanics makes a stronger appeal than the matrix mechanics, because it seems to provide the possibility of an image of the processes involved, and does not rely exclusively on operations carried out by means of mathematical symbols which convey no definite physical idea.

In this connection it is of interest to recall the suggestive work of Carl A. Bjerknes, which has been extended and generalized by his son, V. Bjerknes.* In experiments exhibited at the Paris Electrical Exhibition of 1881 most of the well-known actions between currents and magnets were imitated by means of bodies pulsating and vibrating in water and other fluids. "A very remarkable analogy became evident between the field of motion in a fluid and the electric or magnetic field of force: the bodies produced fields of motion of precisely the same geometric structure as static or stationary electric or magnetic fields. Moreover, they exert apparent actions-at-a-distance upon each other, equal to, but—most curiously—opposite to the actions-at-a-distance between the corresponding bodies in the electric or magnetic fields." The analogy may be pursued in the most minute details, but it is necessary to emphasize the fact that although there is a direct *geometric* analogy between the hydrodynamic field and the electric or magnetic field, the *dynamic* analogy is inverse.

In the new wave theory of matter the material point is conceived as a singularity in a wave. The chief difference between the work of de Broglie and that of Schrödinger is that the former is dealing with progressive waves, while the latter is thinking of stationary wave motion.

"With de Broglie the concept of the electron or other element of energy is primary, whilst that of the phase-wave is secondary, but with Schrödinger the position is reversed. In his theory the principal part is played by the so-called wave-function ψ , which determines the phase-waves and is a solution of a linear partial differential equation of the second order of the type of the wave-equation in classical mathematical physics. The electron, or element of energy, becomes merely a focus of a group of phase-waves, and in the atom, where the focus is ill-defined, it loses its individuality altogether. In order to re-establish contact with electro-dynamics, Schrödinger finds it necessary to introduce a new and at first sight arbitrary hypothesis defining the density of electric charge in terms of the wave-function, but justified by the results to which it has led." †

* V. K. F. Bjerknes, *Nature*, vol. 114, p. 472, 1924.

† G. A. Schott, *Nature*, vol. 119, p. 820, 1927.

As we have seen Schrödinger starts from the idea suggested by de Broglie that an atomic system is not to be represented by a trajectory, i.e., by a point moving through the co-ordinate space but must be represented by a wave in this space. From this starting-point he develops a wave-theory of matter, and obtains from a variation principle a differential equation which the wave function must satisfy. This equation turns out to be closely connected with the Hamiltonian dynamical equation which specifies the system. When the general solution of this equation is known, matrices to represent the canonical variables may easily be obtained satisfying all the conditions that they have to satisfy according to Heisenberg's matrix mechanics. The mathematical equivalence of the theories is thus established, and it is shown that, in the words of Schrödinger, "the wave-mechanics and the matrix mechanics are mathematically identical." The concept of characteristic oscillations in the atom and Schrödinger's theory based upon it represent a most significant contribution to the development of the quantum theory. "From the formal mathematical point of view it includes the whole of the Heisenberg-Born-Dirac matrix theory and gives, moreover, a simplified, practically convenient method of finding the matrices. Beyond this, it opens new avenues of thought and seems to afford our first glimpse of the true nature of the quanta" (Epstein).

Although it is impossible in a single paragraph to do justice to the important work of A. N. Whitehead,* some reference must be made to it here because of the close relationship it bears to the theories advanced in this volume and in particular to the new undulatory mechanics. Whitehead has developed what he calls the *organic* theory of nature: a complete organism in the organic theory corresponds to a bit of material on the materialistic theory. A *primate* may be described briefly as a primary organism which is not decomposable into subordinate organisms. "There are certain indications in modern physics that for the rôle of corpuscular organisms at the base of the physical field, we require vibratory entities. Such corpuscles would be the corpuscles detected as expelled from the nuclei of atoms, which then dissolve into waves of light." "A proton, and perhaps an electron, would be an association of such primates, superposed on each other, with their frequencies and spatial dimensions so arranged as to promote the stability of the complex organism, when jolted into acceleration of locomotion." The conception may be made clearer by means of an analogy from sound or from

* A. N. Whitehead, *The Concept of Nature; An Enquiry concerning the Principles of Natural Knowledge; Science and the Modern World* (Chap. VIII, "The Quantum Theory"); Cambridge University Press.

light. "A steadily sounding note is explained as the outcome of vibrations in the air: a steady colour is explained as the outcome of vibrations in æther. If we explain the steady endurance of matter on the same principle, we shall conceive each primordial element as a vibratory ebb and flow of an underlying energy, or activity. Suppose we keep to the physical idea of energy; then each primordial element will be an organized system of vibratory streaming of energy. Accordingly there will be a definite period associated with each element; and within that period the stream-system will sway from one stationary maximum to another stationary maximum—or, taking a metaphor from the ocean tides, the system will sway from one high tide to another high tide. This system, forming the primordial element, is nothing at any instant. It requires its whole period in which to manifest itself. In an analogous way, a note of music is nothing at an instant, but it also requires its whole period in which to manifest itself." The theory of a primate as a vibrating pattern is shown to be in harmony with the ideas of the quantum theory, and to lead to the locomotion of the primate being regarded as discontinuous in space and time. "The path in space of such a vibratory entity—where the entity is constituted by the vibrations—must be represented by a series of detached positions in space." "If we go below the quanta of time which are the successive vibratory periods of the primate, we find a succession of vibratory electromagnetic fields, each stationary in the space-time of its own duration. Each of these fields exhibits a single complete period of the electromagnetic vibration which constitutes the primate." According to Whitehead the cosmological outlook which he adopts is perfectly consistent with the demands for discontinuity which have been urged from the side of physics.

5. Conclusion

The final judgment passed upon any scientific theory involves a certain æsthetic element which influences our decision. "A theory may predict much that is true and nothing that is false; there may be no alternative proposed which achieves as much; and yet it is perfectly legitimate to reject the theory without hesitation because it fails to give that intellectual satisfaction which is the only end and aim of science."* As regards the quantum theory we cannot but admit that there has been brilliant success in co-ordinating a host of experimental facts; we must admit, too, that it has afforded a certain measure of

* N. R. Campbell, *Modern Electrical Theory*, Chap. XVI, "Relativity," p. 113, 1923.

intellectual satisfaction, and yet it would be premature to come to a definite decision as to the form the theory will ultimately assume.

In the foregoing pages some of the difficulties still to be overcome have been pointed out, and a number of suggestions have been made as to possible interpretations of the quantum. But the scientific student cannot be satisfied with mere speculations, for, in the words of Max Planck: "Our aspiration after a uniform theory of nature, on a mechanical basis or otherwise . . . can never be permanently repressed." We may with confidence anticipate the day when the constitution of the proton and the electron, the structure of the electromagnetic field, and the nature of light shall stand more clearly revealed through the elucidation of the principles of the quantum theory.

In the rapid developments which are taking place at the present time in the field of experimental and theoretical physics we may trace a parallel to the growth of philosophical ideas as recorded by Benedetto Croce.

"To-day I observe in my own case the impossibility of resting upon the results of past thought: I see a new crop of problems springing up in a field from which I have but now reaped a harvest of solutions; I find myself calling in question the conclusions to which I have previously come; and these facts, which appear in every part of philosophy as I handle and rehandle it, force me to recognize that truth will not let itself be tied fast for ever. They teach me modesty towards my present thoughts, which to-morrow will appear deficient and in need of correction, and indulgence towards my self of yesterday or the past, whose thoughts, however inadequate in the eyes of my present self, yet contained some real element of truth; and this modesty and indulgence pass into a sense of piety towards thinkers of the past, whom now I am careful not to blame, as once I blamed them, for their inability to do what no man, however great, can do—to close the eternal gates of truth, to fix into eternity the fleeting moment."

APPENDIX I

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APPENDIX II

FUNDAMENTAL PHYSICAL CONSTANTS

		$\log_{10}$
Electron charge	$e=4.774 \times 10^{-10}$ E.S.U.	$\overline{10.67888}$
Specific electron charge	$e/m=1.761 \times 10^7$ E.M.U./gm.	$\overline{7.24576}$
Mass of electron	$m=9.04 \times 10^{-28}$ gm.	$\overline{28.95620}$
Mass of hydrogen atom	$M=1.649 \times 10^{-24}$ gm.	$\overline{24.21722}$
Avogadro's constant	$N=6.062 \times 10^{23}$ mole. ⁻¹	$\overline{23.78262}$
Gas constant for 1 mole	$R=8.315 \times 10^7$ ergs/gm. deg.	$\overline{7.91986}$
Boltzmann's constant, R/N	$k=1.372 \times 10^{-16}$ ergs/deg.	$\overline{16.13724}$
Constant of molecular energy, $3R/2N$	$a=2.058 \times 10^{-16}$ ergs/deg.	$\overline{16.31333}$
Kinetic energy at 0° C. of a molecule	$w_0=5.619 \times 10^{-14}$ ergs	$\overline{14.74965}$
Velocity of light	$c=2.9986 \times 10^{10}$ cm. sec. ⁻¹	$\overline{10.47692}$
Planck's constant	$h=6.558 \times 10^{-27}$ erg sec.	$\overline{27.81677}$
Fine structure constant	$\alpha=7.282 \times 10^{-3}$	$\overline{3.86225}$
Rydberg constant	$N_H=109677.6$ cm. ⁻¹	$\overline{5.04012}$
	$N_\infty=109737.3$ cm. ⁻¹	$\overline{5.04035}$
Rydberg frequency	$\nu_H=3.2888 \times 10^{15}$ sec. ⁻¹	$\overline{15.51704}$
	$\nu_\infty=3.2906 \times 10^{15}$ sec. ⁻¹	$\overline{15.51727}$
Quantum unit of length	$a_1=0.531 \times 10^{-8}$ cm.	$\overline{9.72509}$
Grating constant, calcite	$d=3.029 \times 10^{-8}$ cm.	$\overline{8.48130}$

APPENDIX III

PLANCK'S RADIATION FORMULA

Formulae for determining the distribution of energy throughout the spectrum may be expressed either in terms of the wave-length λ , or the frequency ν .

We give below formulae for the space density of the energy of uniform monochromatic unpolarized radiation on the classical theory (Rayleigh), and on the quantum theory (Planck). To find the corresponding expressions for plane-polarized radiation, the results must be divided by $8\pi/c$, where c is the velocity of light.

In terms of wave-length :

$$E_{\lambda} d\lambda = 8\pi k T \lambda^{-4} d\lambda, \quad \text{Rayleigh ;}$$

$$E_{\lambda} d\lambda = \frac{8\pi ch}{\lambda^5} \frac{1}{e^{ch/k\lambda T} - 1} d\lambda, \quad \text{Planck.}$$

In terms of frequency :

$$E_{\nu} d\nu = \frac{8\pi \nu^2}{c^3} k T d\nu, \quad \text{Rayleigh ;}$$

$$E_{\nu} d\nu = \frac{8\pi}{c^3} \frac{h \nu^3}{e^{h\nu/kT} - 1} d\nu, \quad \text{Planck.}$$

In these formulae, k is Boltzmann's constant and T is the absolute temperature. If we write x for $h\nu/kT$, Planck's formula differs from Rayleigh's through the presence of the factor $x/(e^x - 1)$. For *large* values of λT Planck's formula becomes identical with Rayleigh's.

For *small* values of λT it becomes $\frac{8\pi ch}{\lambda^5} e^{-ch/k\lambda T}$ which expresses Wien's law of energy distribution.

APPENDIX IV

QUANTIZED ELLIPTIC ORBITS

In the original presentation of Bohr's theory the electron was supposed to be revolving round a positive nucleus in a circular orbit. This is equivalent to treating the atomic system as a system with one degree of freedom only. In a more complete treatment the system must be regarded as having more than one degree of freedom, and thus we are led to an application of the generalized form of the quantum theory to the motion of an electron round the nucleus. This extension of Bohr's theory to the case in which the orbit is in the form of an ellipse was made independently by Sommerfeld* and W. Wilson.† It is found that the size and shape of the ellipse now depend upon *two* integers, n_ϕ and n_r , the first introduced by the application of the quantum relation to the angular motion, the second by the application of the relation to the radial motion.

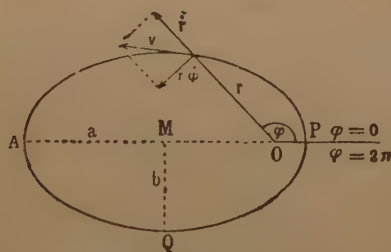


FIG. 30.—Elliptic Orbit.

We consider, then, a nucleus of very great mass (carrying a charge $+e$), and an electron of smaller mass (carrying a charge $-e$). In the case of the electron we shall, for the present at any rate, neglect the variation of mass with speed required by the principle of relativity. Under these conditions the electron describes an elliptic orbit with the nucleus at one focus. The motion resembles the motion of a planet round the sun, discussed by Kepler and treated mathematically by Newton. The co-ordinates of the electron are r, ϕ , using polar co-ordinates with the focus as origin. The components of the velocity are $\dot{r}$ and $r\dot{\phi}$.

* Sommerfeld, *Ann. d. Physik*, vol. 51, p. 1, 1916.

† W. Wilson, *Phil. Mag.*, vol. 31, p. 161, 1916.

One first integral of the equations of motion expresses the fact that the angular momentum is constant. That is

$$mr^2\dot{\phi} = \text{constant} = p \quad . \quad . \quad . \quad (1)$$

corresponding to the second of Kepler's laws. The equation of the ellipse (eccentricity ϵ , semi latus rectum l) may be written in this form

$$\begin{aligned} \sigma = \frac{1}{r} &= \frac{me^2}{p^2}(1 + \epsilon \cos \phi) \\ &= \frac{1}{l}(1 + \epsilon \cos \phi) \quad . \quad . \quad . \quad (2) \end{aligned}$$

an ordinary analytical expression for an ellipse in polar co-ordinates ϕ being taken as zero at perihelion.

The kinetic energy of the moving electron is

$$T = \frac{m}{2}(\dot{r}^2 + r\dot{\phi}^2) \quad . \quad . \quad . \quad (3)$$

But
$$\dot{r} = \dot{\phi} \frac{dr}{d\phi} = \frac{p}{mr^2} \frac{dr}{d\phi} = -\frac{p}{m} \frac{d\sigma}{d\phi} = \frac{e^2}{p} \epsilon \sin \phi \quad . \quad . \quad . \quad (4)$$

and
$$r\dot{\phi} = \frac{p}{mr} = \frac{p}{m} \sigma = \frac{e^2}{p}(1 + \epsilon \cos \phi) \quad . \quad . \quad . \quad (5)$$

Hence
$$T = \frac{me^4}{2p^2}(1 + 2\epsilon \cos \phi + \epsilon^2) \quad . \quad . \quad . \quad (6)$$

The potential energy is

$$V = -\frac{e^2}{r} = -\frac{me^4}{p^2}(1 + \epsilon \cos \phi) \quad . \quad . \quad . \quad (7)$$

The total energy, $H = T + V$

$$= -\frac{me^4}{2p^2}(1 - \epsilon^2) \quad . \quad . \quad . \quad (8)$$

and is constant as it should be.

So we find
$$W = -H = \frac{me^4}{2p^2}(1 - \epsilon^2) \quad . \quad . \quad . \quad (9)$$

The Quantum Relations.—We now have to introduce the restrictions imposed by the quantum theory on the possible orbits. The expressions obtained for the energy show that the polar co-ordinates ϕ, r are canonical co-ordinates in the Hamiltonian sense, and may be regarded as equivalent to q_1, q_2 in the equations of restriction (p. 22).

We consider first the co-ordinate ϕ , and "quantize with respect to the angular motion" only, that is we impose the restriction expressed by the equation

$$\int_0^{2\pi} p_\phi d\phi = p \int_0^{2\pi} d\phi = 2\pi p = n_\phi h \quad . \quad . \quad (10)$$

According to quantum mechanics the angular momentum must be an integral multiple of $h/2\pi$, which is the same condition as we

had previously for the circular motion. This would mean that

$$W = \frac{h\nu_{\infty} (1 - \varepsilon^2)}{n_{\phi}^2},$$

and the frequency of the emitted radiation would, according to Bohr's frequency condition, be determined by

$$\begin{aligned} h\nu &= W_e - W_a \\ &= h\nu_{\infty} \left(\frac{1 - \varepsilon_e^2}{n_e^2} - \frac{1 - \varepsilon_a^2}{n_a^2} \right) \quad \dots \quad (I1) \end{aligned}$$

In this equation the eccentricities, ε_e , and ε_a could assume all possible values, and thus, as Sommerfeld points out, we should find not a series of discrete lines but a diffuse band.

We have, however, now to consider the restrictions imposed with regard to the radial motion, or to "quantize with respect to the variable r ." The quantum condition in this case is

$$\int p_r dr = n_r h \quad \dots \quad (I2)$$

where p_r refers to the "moment" or the "impulse" corresponding to the co-ordinate r , and the integration must extend from the minimum value of r to the maximum and back again to the minimum. The value of $p_r = m\dot{r}$, the momentum in the direction of the radius vector, so we have

$$\int p_r dr = \int m\dot{r} dr = \int_0^{2\pi} m\dot{r} \frac{dr}{d\phi} d\phi = n_r h \quad \dots \quad (I3)$$

We must now express this quantity to be integrated in terms of ϕ and ε , the eccentricity of the ellipse.

From (4) we have

$$m\dot{r} = \frac{me^2\varepsilon}{p} \sin\phi \quad \dots \quad (I4)$$

and from (2)

$$\frac{dr}{d\phi} = \frac{p^2\varepsilon}{me^2} \frac{\sin\phi}{(1 + \varepsilon\cos\phi)^2} \quad \dots \quad (I5)$$

Hence

$$\begin{aligned} n_r h &= p\varepsilon^2 \int_0^{2\pi} \frac{\sin\phi}{(1 + \varepsilon\cos\phi)^2} d\phi \\ &= 2\pi p \left(\frac{1}{\sqrt{1 - \varepsilon^2}} - 1 \right) \quad \dots \quad (I6) \end{aligned}$$

Since $2\pi p = nh$, the eccentricity is determined by

$$1 - \varepsilon^2 = \frac{n_{\phi}^2}{(n_{\phi} + n_r)^2} \quad \dots \quad (I7)$$

or

$$\varepsilon^2 = \frac{(2n_{\phi} + n_r)n_r}{(n_{\phi} + n_r)^2} \quad \dots \quad (I8)$$

This means that not only the angular momentum, but also the eccentricity can have only certain prescribed values.

The expression for the energy, W , may now be written in terms of n_ϕ and n_r

$$W = \frac{2\pi^2 m e^4}{h^2} \frac{1}{(n_\phi + n_r)^2} = \frac{2\pi^2 m e^4}{h^2} \frac{1}{n^2} \quad . \quad . \quad . \quad (19)$$

so that the important fact emerges from this result that the energy depends only on the *sum* of the two integers of n_ϕ and n_r . These integers, for convenience, may be referred to as the "azimuthal quantum number," and the "radial quantum number," respectively. The energy depends on the "total quantum number," n , which is the sum of these partial quantum numbers n_ϕ and n_r .

The frequency of the radiation emitted is given by

$$\nu = \nu_\infty \left(\frac{1}{n_s^2} - \frac{1}{n_a^2} \right) \quad . \quad . \quad . \quad . \quad (20)$$

We thus obtain the Balmer series, and other associated series, for hydrogen, just as before; but the series will now be composed of sharply defined lines. Since the total quantum number can be made up in various ways, each line can be obtained by the passage of an electron from several different orbits, which can be elliptic or circular, to some inner orbit.

It is easy to show that the semi-axes a and b of the elliptic orbit are given by

$$a = \frac{h^2}{4\pi^2 m e^2} (n_\phi + n_r)^2, \quad b = \frac{h^2}{4\pi^2 m e^2} n_\phi (n_\phi + n_r) \quad . \quad . \quad (21)$$

When $n_r = 0$, we get the circles of Bohr's theory. We may notice that all orbits having the same value for the energy have equal major axes, in fact $W = e^2/2a$. Again, the frequency of the electron in its orbit is given by

$$\bar{\nu} = \frac{\dot{\phi}}{2\pi a b m} = \frac{4\pi^2 m e^4}{h^3 (n_\phi + n_r)^3} = \frac{2\nu_\infty}{(n_\phi + n_r)^3} \quad . \quad . \quad . \quad (22)$$

where ν_∞ is the fundamental Rydberg frequency.

From equations (19) and (22) we see that W may be expressed in the simple form

$$W = \frac{1}{2} (n_\phi + n_r) h \bar{\nu} \quad . \quad . \quad . \quad . \quad (23)$$

APPENDIX V

TABLE OF ELECTRON GROUPS IN THE CHEMICAL ELEMENTS

(Reproduced from Fowler's Presidential Address to Section A of the British Association, Section A, 1926.)

ARRANGEMENT OF ELECTRONS IN ATOMS.

N.B.—For convenience in printing the half quantum numbers in column 4 have all been increased by $\frac{1}{2}$: See pp. 63 and 81.

Period	Atomic Number	Element	Spectroscopic Term, l	Number of Electrons in Shell of Quantum Number n_{kk}											
				K 1 ₁₁	L _I 2 ₁₁	L _{II} 2 ₂₁	L _{III} 2 ₂₂	M _I 3 ₁₁	M _{II} 3 ₂₁	M _{III} 3 ₂₂	M _{IV} 3 ₃₂	M _V 3 ₃₃	N _I 4 ₁₁	N _{II} 4 ₂₁	N _{III} 4 ₂₂
1	1	H		1											
	2	He	$1S_0^*$	2											
	3	Li	$2S_1^*$	2	1										
	4	Be	$1S_0^*$	2	2										
	5	B	$2P_1^*$	2	2	1									
	6	C	$3P_0^*$	2	2	2									
	7	N	$4S_2^*$	2	2	2	1								
	8	O	$3P_2^*$	2	2	2	2								
	9	F	$2P_2^*$	2	2	2	3								
	10	Ne	$1S_0^*$	2	2	2	4								
3	11	Na	$2S_1^*$	2	2	2	4	1							
	12	Mg	$1S_0^*$	2	2	2	4	2							
	13	Al	$2P_1^*$	2	2	2	4	2	1						
	14	Si	$3P_0^*$	2	2	2	4	2	2						
	15	P	$4S_2^*$	2	2	2	4	2	2	1					
	16	S	$3P_2^*$	2	2	2	4	2	2	2					
	17	Cl	$2P_2^*$	2	2	2	4	2	2	3					
	18	A	$1S_0^*$	2	2	2	4	2	2	4					
4	19	K	$2S_1^*$	2	2	2	4	2	2	4			1		
	20	Ca	$1S_0^*$	2	2	2	4	2	2	4			2		
	21	Sc	$2D_2^*$	2	2	2	4	2	2	4	1		2		
	22	Ti	$3F_2^*$	2	2	2	4	2	2	4	2		2		
	23	V	$4F_2^*$	2	2	2	4	2	2	4	3		2		
	24	Cr	$7S_3^*$	2	2	2	4	2	2	4	4	1	1		
	25	Mn	$6S_3^*$	2	2	2	4	2	2	4	4	1	2		
	26	Fe	$5D_1^*$	2	2	2	4	2	2	4	4	2	2		
	27	Co	$4F_5^*$	2	2	2	4	2	2	4	4	3	2		
	28	Ni	$3F_4^*$	2	2	2	4	2	2	4	4	4	2		
	29	Cu	$2S_1^*$	2	2	2	4	2	2	4	4	6	1		
	30	Zn	$1S_0^*$	2	2	2	4	2	2	4	4	6	2		
	31	Ga	$2P_1^*$	2	2	2	4	2	2	4	4	6	2		
	32	Ge	$3P_0^*$	2	2	2	4	2	2	4	4	6	2	1	
	33	As	$4S_1^*$	2	2	2	4	2	2	4	4	6	2	2	1
	34	Se	$3P_2^*$	2	2	2	4	2	2	4	4	6	2	2	2
	35	Br	$2P_2^*$	2	2	2	4	2	2	4	4	6	2	2	3
	36	Kr	$1S_0^*$	2	2	2	4	2	2	4	4	6	2	2	4

ARRANGEMENT OF ELECTRONS IN ATOMS—(Continued).

K, L, and M Shells like Kr Complete with 28 Electrons.

Period	Atomic Number	Element	Spectroscopic Term, r, l	Number of Electrons in Shell of Quantum Number $n_{kk'}$												
				N_I	N_{II}	N_{III}	N_{IV}	N_V	N_{VI}	N_{VII}	O	O_I	O_{II}	O_{IV}	P_I	
				4 ₁₁	4 ₂₁	4 ₃₃	4 ₃₃	4 ₃₃	4 ₆₃	4 ₄₄	5 ₁₁	5 ₂₁	5 ₂₃	5 ₃₃	6 ₁₁	
5	37	Rb	$2S_1^*$	2	2	4						I				
	38	Sr	$1S_0^*$	2	2	4						2				
	39	Y	$2D_3^*$	2	2	4	I					2				
	40	Zr	$3F_3^*$	2	2	4	2					2				
	41	Nb	$6D_1^*$	2	2	4	4					I				
	42	Mo	$7S_3^*$	2	2	4	4	I				I				
	43	Ma	$6D_4^*$	2	2	4	4	(2)-				(I)				
	44	Ru	$5F_5^*$	2	2	4	4	3				I				
	45	Rh	$4F_5^*$	2	2	4	4	4				I				
	46	Pd	$1S_0^*$	2	2	4	4	6								
	47	Ag	$2S_1^*$	2	2	4	4	6				I				
	48	Cd	$1S_0^*$	2	2	4	4	6				2				
	49	In	$2P_1^*$	2	2	4	4	6				2	I			
	50	Sn	$3P_0^*$	2	2	4	4	6				2	2			
6	51	Sb	$4S_2^*$	2	2	4	4	6				2	2	I		
	52	Te	$3P_2^*$	2	2	4	4	6				2	2	2		
	53	I	$2P_3^*$	2	2	4	4	6				2	2	3		
	54	Xe	$1S_0$	2	2	4	4	6				2	2	4		
	55	Cs	$2S_1^*$	2	2	4	4	6				2	2	4		I
	56	Ba	$1S_0^*$	2	2	4	4	6				2	2	4		2
	57	La	$2D_3$	2	2	4	4	6				2	2	4	I	2
	58	Ce	$3H_4$	2	2	4	4	6	I			2	2	4	I	2
	59	Pr	$4K_6$	2	2	4	4	6	2			2	2	4	I	2
	60	Nd	$5L_6$	2	2	4	4	6	3			2	2	4	I	2
	61	Il	$6L_6$	2	2	4	4	6	4			2	2	4	I	2

ARRANGEMENT OF ELECTRONS IN ATOMS—(Continued).

K, L, M and N Shells like Lu Complete with 60 Electrons.

Period	Atomic Number	Element	Spectroscopic Term, r, l_f	Number of Electrons in Shell of Quantum Number nkl									
				O _I 5 ₁₁	O _{II} 5 ₂₁	O _{III} 5 ₂₂	O _{IV} 5 ₃₂	O _V 5 ₃₃	P _I 6 ₁₁	P _{II} 6 ₂₁	P _{III} 6 ₂₂	P _{IV} 6 ₃₂	Q _I 7 ₁₁
	72	Hf	3F_2	2	2	4	2		2				
	73	Ta	4F_2	2	2	4	3		2				
	74	W	$^5D_0^*$	2	2	4	4		2				
	75	Re	6S_3	2	2	4	4	1	2				
			6D_5					2	1				
	76	Os	5D_4	2	2	4	4	2	2				
			5F_5					3	1				
	77	Ir	4F_5	2	2	4	4	3	2				
			4F_5					4	1				
	78	Pt	3D_3	2	2	4	4	5	1				
	79	Au	$^2S_1^*$	2	2	4	4	6	1				
	80	Hg	$^1S_0^*$	2	2	4	4	6	2				
	81	Tl	$^3P_1^*$	2	2	4	4	6	2	1			
	82	Pb	$^3P_0^*$	2	2	4	4	6	2	2			
	83	Bi	4S_3	2	2	4	4	6	2	2	1		
	84	Po	3P_2	2	2	4	4	6	2	2	2		
	85		3P_2	2	2	4	4	6	2	2	3		
	86	Rn	1S_0	2	2	4	4	6	2	2	4		
7	87		2S_1	2	2	4	4	6	2	2	4		1
	88	Ra	1S_0	2	2	4	4	6	2	2	4		2
	89	Ac	2D_3	2	2	4	4	6	2	2	4	(1)	(2)
	90	Th	3F_3	2	2	4	4	6	2	2	4	(2)	(2)
	91	PAc	4F_3	2	2	4	4	6	2	2	4	(3)	(2)
	92	U	5D_0	2	2	4	4	6	2	2	4	(4)	(2)



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